March 15, 1966

Interim Report No. 2 | *August 1965 to March 1966*

POLYMERS FOR SPACECRAFT HARDWARE--MATERIALS SPECIFICATIONS AND ENGINEERING INFORMATION

Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA 91103

JPL CONTRACT NO. 950745
UNDER NAS7-100

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SRI Project No. ASD-5046

Approved: R. F. MURACA, DIRECTOR
ANALYSES AND INSTRUMENTATION

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FOREWORD

This Interim Report summarizes the work performed by Stanford Research Institute during the period August 1965 to March 1966 under Contract No. 950745 for the Jet Propulsion Laboratory of the California Institute of Technology.

Cognizant Engineers of the Jet Propulsion Laboratory's Materials and Methods Group were Mr. Hugh G. Maxwell, Phase I - Materials Specifications, and Mr. Robert Harrington, Phase II - Engineering Information.

The technical effort at Stanford Research Institute was under the supervision of Dr. R. F. Muraca, Director, Analyses and Instrumentation. Personnel responsible for the performance, guidance, and evaluation of work were: N. Fishman, Manager, Propellants Evaluation; H. G. Thomas, Supervisor, Analytical Services, and J. S. Whittick, Chemist-Program Coordinator.

Acknowledgment is made of the work of a number of chemists, technicians, and machinists who have contributed to this program. Special mention is made of the efforts of R. Won, Chemist, in the development of specification test methods.

ABSTRACT

Stanford Research Institute, Menlo Park, California
POLYMERS FOR SPACECRAFT HARDWARE - MATERIALS SPECIFICATIONS AND ENGINEERING INFORMATION
Interim Report No. 2, August 1965 to March 1966
R. F. Muraca, et al., March 15, 1966
(NASA Contract No. NAS7-100; JPL Contract 950745; SRI Project ASD-5046)

The objectives of this program are: (1) to provide information on the chemical and physical properties of space polymers so as to permit preparation of procurement specifications; and (2) to obtain new information of the effects of simulated spacecraft environment on candidate space polymers.

Test methods are discussed for the chemical and physical properties of epoxy adhesives and RTV-silicone rubbers (including curing agents). Results for typical polymeric materials and the details for suggested specification test-methods are also given.

A standardized procedure for thermal-vacuum weight-loss of polymeric materials is described; results are given for 20 polymeric materials, and weight-loss limits for materials are suggested.

Units for the determination of volatile condensable material (VCM) are described; these units will provide engineering information on VCM but they have not been put into service at this time. A micro-VCM unit, designed to screen polymeric materials, is in operation; available data on VCM, as well as weight-loss are given. The results of mass spectrometric studies of substances volatilized from typical space polymers are presented.

Discussion is made of the *in situ* measurements of mechanical properties of a series of elastomers and plastics; data are provided on the progress of the 8-month storage tests under constant strain for selected elastomers.

In accordance with the "New Technology Clause," four disclosures are made of advancement of technology under JPL/NASA sponsorship.

A table summarizing the work performed on a group of polymers is given in the Appendix.

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ILLUSTRATIONS (Concluded)

INTRODUCTION

This Interim Report summarizes the work performed under JPL Contract 950745, SRI Project ASD-5046, during the period August 1965 to March 1966.

The primary objectives of this program are to assist the Jet Propulsion Laboratory of the California Institute of Technology in the development and preparation of polymeric material specifications to be used in connection with JPL spacecrafts, and to provide a study of the effects of simulated space environment on selected commercial polymeric products. The materials and products to be studied and the extent of work to be performed are specified by the JPL Cognizant Engineers.

The program is conducted as two interrelated and concurrent phases: The purpose of Phase I, Polymeric Materials Specifications, is to obtain quantitative values for parameters which may be used to assure the performance of a given batch of material in a spacecraft environment. The purpose of Phase II, Engineering Information, is to establish material limitations and to obtain detailed design information.

Section I of this report summarizes a number of chemical and physical test methods which have been evaluated for incorporation into specifications, and lists the results obtained with typical polymeric materials. In many instances, ASTM methods have been found adequate; in other instances, test methods have been developed or adopted from suggestions made in the chemical literature or in manufacturer's literature.

In Section II, details are given of test methods which have been developed, adopted, or modified at SRI. All of these methods have been forwarded to the JPL Cognizant Engineer as suggestions for inclusion in specifications test requirements.

A review of the vacuum-weight-loss apparatus and the work leading to the formulation of a standardized procedure for weight-loss determinations is given in Section III. Also included are weight-loss results for 20 polymeric materials, some of which were re-determined subsequent to simple postcuring treatments. A table of weight-loss limits for selected polymers (less than 1% weight-loss) is also given.

Section IV includes a discussion of the in situ mechanical-property measurements conducted in a thermal-vacuum environment and describes the work performed: the most recent results for the elastomers which are being subjected to constant strain for an 8-month period in the vacuum-thermal environment are tabulated.

In Section V, fabrication of an improved VCM apparatus is described. Additionally, details are given of the design and operation of a micro-VCM apparatus which provides data for maximum VCM available as well as weight-loss-data; this unit is to be used as to screen polymeric materials for both phases of the JPL program.

The identification by mass spectrometry of volatilized substances from a series of polymeric materials is discussed in Section V.

In subsequent Sections, "Future Work" is described in general terms, and "New Technology" provides pertinent information on technologies which have been advanced or developed under the JPL/NASA sponsorship of this program. A table summarizing the work performed on the group of polymers examined thus far is given in the Appendix.

PHASE I

MATERIALS SPECIFICATIONS

I. CHEMICAL AND PHYSICAL TEST METHODS FOR SPECIFICATIONS

Materials specifications are, in general, prepared to provide a degree of quality-control for acceptable materials and to establish numerical norms for values of certain parameters in order to provide standards for new materials. Work performed toward the development and preparation of specifications for polymeric materials to be used in spacecrafts has included the selection of meaningful physical and chemical properties, the evaluation of test methods, and the analyses of representative spacecraft polymers in order to provide limits for selected properties.

The selection of properties and test methods was made subsequent to a study of polymer chemistry and synthetic procedures for each polymer class in the light of assuring conformance of the polymers with end-use requirements. The test methods which have been recommended for specifications are, for the most part, methods which are easily performed in nearly any chemical laboratory. The polymeric materials which have been evaluated were selected by the JPL Cognizant Engineer.

The establishment of test methods for epoxy adhesives has been completed, and methods for RTV-type silicone potting compounds are nearly finalized. ASTM methods have been used and suggested for specifications wherever possible; it has been found that although a test method is applicable to a general class of polymers, some modification may be required for specific polymer products. Details of procedures other than ASTM, or modifications thereof, are given in Section II of this report. The incorporation of suggested test methods into JPL Specifications has been discussed and reviewed with the JPL Cognizant Engineer.

A. EPOXY ADHESIVES

The results reported in Interim Report No. 1 (August 9, 1965) for a series of epoxy adhesives included epoxy equivalent, hydrolyzable halide content, filler content, nonvolatile content, density, and infrared absorbance spectrum. Since that time, work has been completed for amine-nitrogen content of curing agents Epon 931B and Epon B-3, filler content of Epon 917, and acetone-soluble content of Epon 422J (all supplied by Shell Chemical Company).

Amine Nitrogen Content

Determination of amine-nitrogen content of epoxy curing agents Epon 931B and Epon B-3 was first attempted by ASTM Method D 2073-62T (for fatty amines); however, the titration end-point was found difficult to locate, and the values obtained were suspiciously low. A cross-check by the Dumas micro-procedure for nitrogen corroborated suspicions that the ASTM method gave low results. Subsequent investigation revealed that nonaqueous titrations give satisfactory values for the aromatic amines:

> The sample is dissolved in glacial acetic acid and the amine groups are titrated with a solution of perchloric acid in glacial acetic acid; methyl violet is used as indicator.

The values obtained for the curing agents by the Dumas nitrogen method and by nonaqueous titration are given in Table I. Also given in Table I is the value for a different batch of Epon B-3. The amine-nitrogen content for the B-3 received in July was below Shell Company specifications of 19-23%; however, a cross-check of this particular batch was conducted at Shell and the value of 18.5% was confirmed. A new batch of B-3, received in September, was found to have a slightly higher amine-nitrogen content, 19.2%, but it was still barely above the lower limits of Shell specifications. The need for specifications standards and procedures is clearly demonstrated by the severe batch-to-batch variations detected above.

Table I

DETERMINATIONS OF AMINE-NITROGEN
IN EPON CURING AGENTS
(Shell Chemical Company)

Material	Amine-Nitrogen Content	
	Dumas Nitrogen (micro-method)	Nonaqueous titration
Epon 931B	24.3%	24.2-24.3%
Epon B-3 (rec'd 7/65)	18.5%	18.5-18.5%
Epon B-3 (rec'd 9/65)	--	19.2%

Filler Content

The filler content of Epon 917 was determined in accordance with Shell Chemical Company Method ADM-3, but low values were obtained. Investigation of the procedure showed that the recommended solvent (chlorobenzene for epoxy-type materials in general) did not dissolve all the organic material present in the adhesive. The results of additional experiments led to the finding that methyl ethyl ketone is a superior solvent for Epon 917 (see Section II, TM-5046-3); appropriate values for filler content are 20.57-20.89 wt-%. It was recommended that methyl ethyl ketone be substituted for chlorobenzene.

Acetone-Soluble Content

It was found that the usual test methods for epoxy resins were not readily applicable to complex formulations such as the adhesive tape Epon 422J (an epoxy-phenolic resin with aluminum filler impregnated on a glass-fiber tape. To circumvent this difficulty, it was decided to use the extractable organic content of the material as a measure of its serviceability. Generally, simple extraction with a suitable solvent is sufficient for removal of organic from inorganic materials (e.g., filler content methods); however, it was found that a Soxhlet extraction of the adhesive tape with acetone was required for accurate results:

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> About 10 g of the epoxy-phenolic adhesive tape is extracted for 4 hours with 250 ml of acetone in a Soxhlet apparatus, and then the Soxhlet thimble and contents are dried overnight at 110°C prior to final weighing.

A relatively large sample must be used in order to compensate for non-uniformities of impregnation. Details of the procedure are given in Section II, TM-5046-4; values obtained for acetone-soluble content of Epon 422J are 42.33-42.87 wt-%.

B. RTV-SILICONE POTTING COMPOUNDS

The following properties (and test methods) have been investigated for RTV-silicone base materials and curing agents: hydrolyzable halide content, hydroxyl content, tin content, nonvolatile content, density, viscosity, and infrared spectra. Suggestions for test methods and limits for most of these properties have been made to the JPL Cognizant Engineer for incorporation into Specifications. A small amount of work remains for tests of cured materials.

Filler Content

Filler content of RTV-11, -60, -560, and -615A (General Electric Company) has been determined by a straightforward procedure involving extraction of the silicone base material with chloroform:

> About 0.3 g of the silicone base material, 50 ml of chloroform, and about 0.3 g of Celite filter-aid are mixed thoroughly; the mixture is filtered and filler content is computed after corrections for Celite.

Details of the procedure are given in Section II, TM-5046-5, and results are summarized in Tables II-V.

Hydrolyzable Halide

Although a chlorinated silane is an intermediate product in the production of silicone polymers, virtually all chloride ion must be absent for qualification of the end-product as a space-grade material, since evolution of chloride ion as chlorine or hydrochloric acid would

be detrimental to spacecraft operations. The following procedure has been used for determination of hydrolyzable halide in the silicones reported in Tables II-V.

> About 5-6 g of silicone base material is treated with 50 ml of ethanol. The resulting solution is titrated potentiometrically with 0.1 N sodium hydroxide; results are reported as wt-% hydrolyzable halide (as chloride).

Details of the procedure are given in Section II, TM-5046-6.

Infrared Spectra

Infrared absorbance curves were obtained for films of the RTV silicones under study and are reproduced in Figures 1-4 (under Tables II-V). The films were prepared by evaporating chloroform extracts of the silicone-base materials on salt flats. Duplicate curves have been forwarded to the JPL Cognizant Engineer for incorporation into Specifications.

Nonvolatile Content

The nonvolatile contents of the RTV materials under study are summarized in Tables II-V. The determinations were made in accordance with ASTM Method D 1259-61(B), i.e., drying resin films on aluminum foil in a forced-draft oven at 105 °C; it was found that better reproducibility of results was obtained if the samples were cooled in a desiccator, rather than simply cooling in air and weighing quickly as specified in the ASTM method.

Viscosity

The viscosity determinations for the RTV base materials are summarized in Tables II-V. The results were obtained in accordance with the modifications to ASTM Method D 1084(B), as modified by the General Electric Company in their Specifications Guide: CDS-373C.

A brief investigation of the effects of de-aerating and conditioning was undertaken; it was found that higher viscosity values were generally obtained if the samples were used as received. Although the higher values

are still within specification limits, it is recommended that the GE modifications be incorporated into the JPL Specifications in order to ensure uniform quality control.

Hydroxyl Content

A review of the literature indicated that a number of procedures had been suggested for determination of the silanol group but that most of them do not provide satisfactory and reproducible results. One of the more promising suggestions, azeotropic distillation of the water of condensation of silicones, was briefly investigated but insufficient water was obtainable even with 100-g samples. Thus, the ASTM procedure, ASTM E 222-63T, "Hydroxyl Groups by Acetic Anhydride Acetylation," was used to obtain the results given in Tables II-V:

> The sample is refluxed with a solution of acetic anhydride in pyridine, excess reagent is hydrolyzed with water, and the acetic acid is titrated with standard sodium hydroxide solution. The end point is determined potentiometrically.

Density

The densities of the silicone base materials, reported in Tables II-V, were determined in accordance with ASTM Method D 1875-61T; all results are in excellent agreement with manufacturer's specifications.

Table II

DETERMINATIONS OF CHEMICAL AND PHYSICAL PROPERTIES:
RTV-11 (General Electric Company)

Property	Test Method	Values
Base Material		
Hydrolyzable halide	TM-5046-6*	0.003-0.005 wt-%
Hydroxyl content	ASTM E 222-63T	0.98-1.10 m.e./g
Filler (TiO_2) content	TM-5046-5*	29.77-29.90 wt-%
Nonvolatile content	ASTM D 1259-61(B)	98.57-98.58 wt-%
Density $^{25}_{4}$	ASTM D 1875-61T	1.161-1.168 g/ml
Viscosity at 25°C (No. 5 spindle, 4 rpm)	ASTM D 1084(B); modified by GE, Spec Guide CDS-373C	91 poises
Catalyst		
T-12 (see Table VI)		

* See Section II

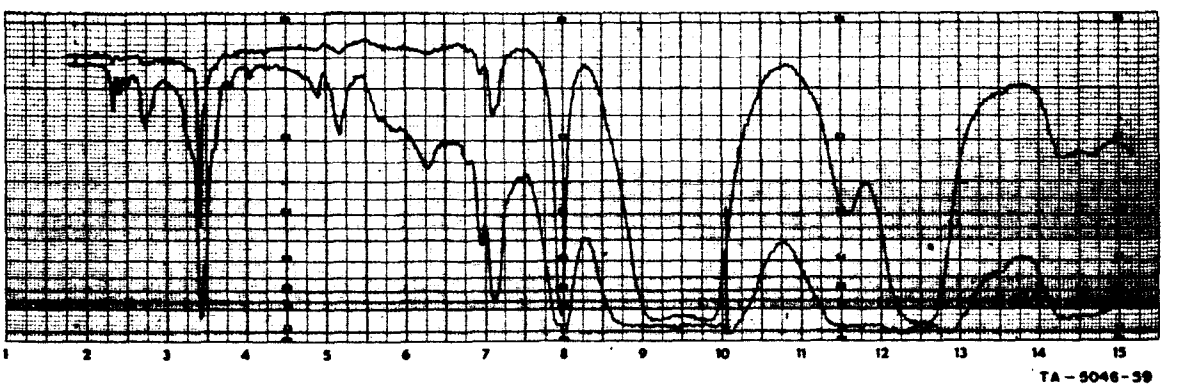

FIG. 1 INFRARED ABSORBANCE SPECTRUM OF RTV-11

Table III

DETERMINATIONS OF CHEMICAL AND PHYSICAL PROPERTIES:
RTV-60 (General Electric Company)

Property	Test Method	Values
Base Material		
Hydrolyzable halide	TM-5046-6*	0.002-0.003 wt-%
Hydroxyl content	ASTM E 222-63T	0.27-0.36 m.e./g
Filler (Fe_2O_3) content	TM-5046-5*	50.08-50.33 wt-%
Nonvolatile content	ASTM D 1259-61(B)	99.20-99.23 wt-%
$Density_4^{25}$	ASTM D 1875-61T	1.476-1.488 g/ml
Viscosity at 25 °C (No. 6 spindle, 10 rpm)	ASTM D 1084(B); modified by GE, Spec Guide CDS-373C	595 poises
Catalyst		
T-12 (see Table VI)		

* See Section II

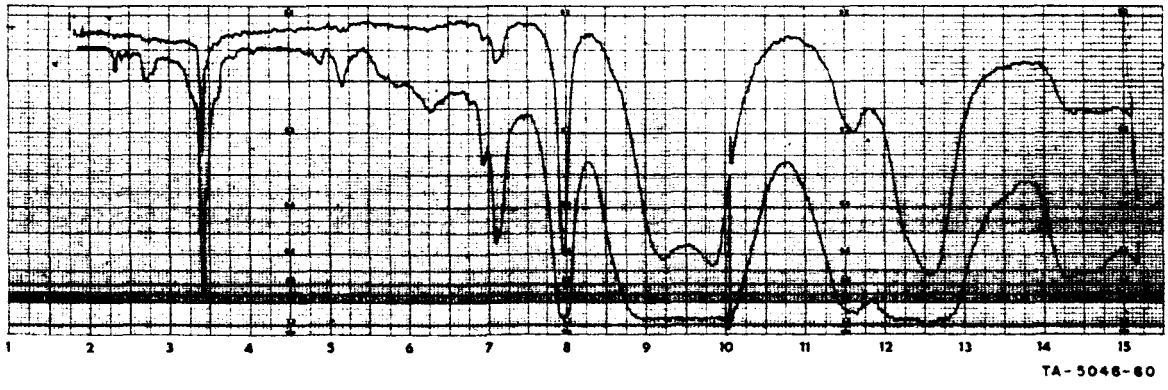

FIG. 2 INFRARED ABSORBANCE SPECTRUM OF RTV-60

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Table IV

DETERMINATIONS OF CHEMICAL AND PHYSICAL PROPERTIES:
RTV-560 (General Electric Company)

Property	Test Method	Values
Base Material		
Hydrolyzable halide	TM-5046-6*	0.004-0.005 wt-%
Hydroxyl content	ASTM E 222-63T	0.19-0.26 m.e./g
Filler (Fe_2O_3) content	TM-5046-5*	42.68-42.71 wt-%
Nonvolatile content	ASTM D 1259-61(B)	98.25-98.47 wt-%
Density$_4^{25}$	ASTM D 1875-61T	1.419-1.425 g/ml
Viscosity at 25°C (No. 6 spindle, 10 rpm)	ASTM D 1084(B); modified by GE, Spec Guide CDS-373C	410 poises
Catalyst		
T-12 (see Table VI)		

* See Section II

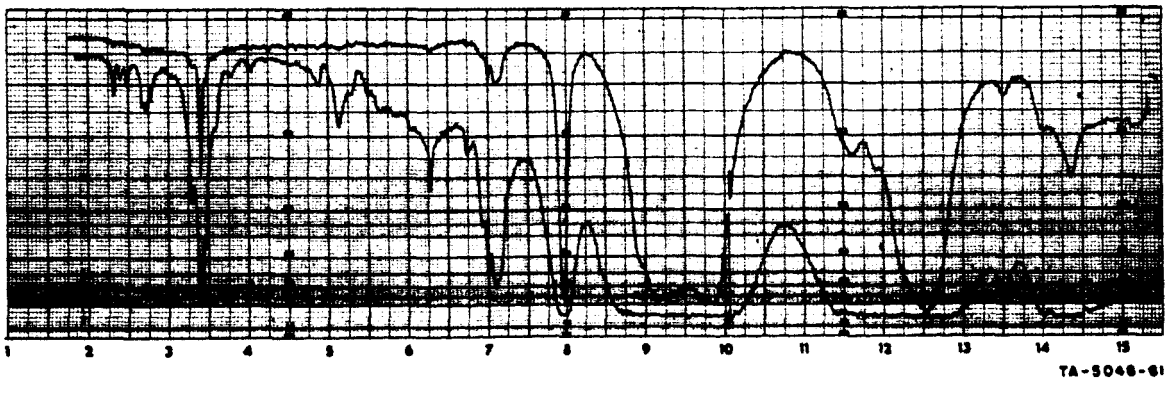

FIG. 3 INFRARED ABSORBANCE SPECTRUM OF RTV-560

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Table V

DETERMINATIONS OF CHEMICAL AND PHYSICAL PROPERTIES:
RTV-615A (General Electric Company)

Property	Test Method	Values
Base Material		
Hydrolyzable halide	TM-5046-6*	0.002-0.002 wt-%
Hydroxyl content	ASTM E 222-63T	0.02-0.05 m.e./g
Filler content	TM-5046-5*	none
Nonvolatile content	ASTM D 1259-61 B	99.66-99.78 wt-%
Density $^{25}_{4}$	ASTM D 1875-61T	1.013-1.015 g/ml
Viscosity at 25°C (No. 5 spindle, 4 rpm)	ASTM D 1084(B); modified by GE, Spec Guide CDS-373C	38 poises
Curing Agent		
615B (see Table VIII)		

* See Section II

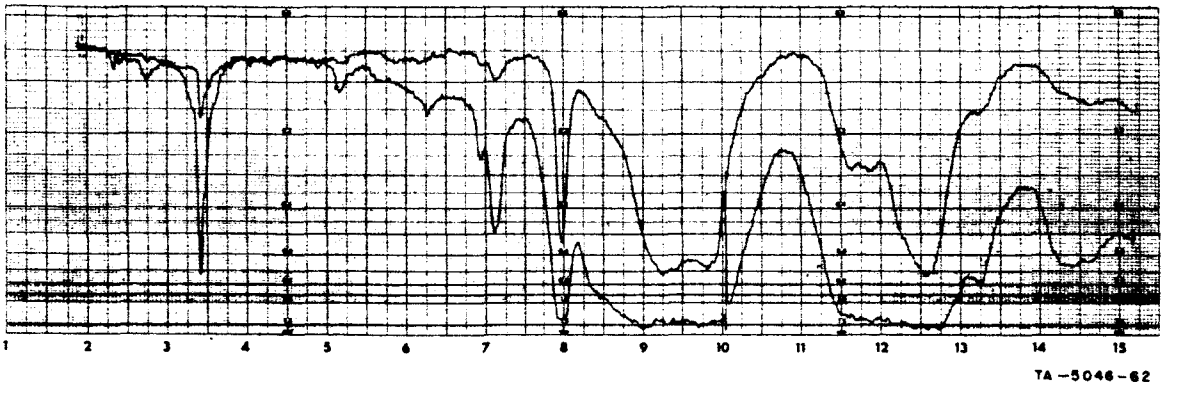

FIG. 4 INFRARED ABSORBANCE SPECTRUM OF RTV-615

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C. M&T CATALYST T-12

The catalyst used for the General Electric RTV-11, -60, and -560 silicone potting compounds is dibutyltindilaurate, marketed by M&T Chemicals, Inc. as M&T Catalyst T-12. Discussion with the JPL Cognizant Engineer established that the most significant properties of this material to be determined for specifications purposes would be hydrolyzable halide content, tin content, density, and viscosity. The results of these determinations are summarized in Table VI.

Hydrolyzable Halide

Hydrolyzable halide content was determined according to the procedure previously described for epoxy adhesives (see Section II, TM-5046-1); no halide was detectable, and thus a specification limit can be recommended as "less than 0.001%."

Tin Content

Evaluation of several methods reported in the chemical literature for the determination of tin in organotin compounds led to a satisfactory procedure for specifications purposes:

> The organotin compound is decomposed by treatment with concentrated sulfuric acid followed by ignition to stannic oxide.

The values given in Table VI are well within the tin content specified by the manufacturer (18-19.5%) and compare favorably with the theoretical value for pure dibutyltindilaurate (18.80%). Details of the procedure are given in Section II, TM-5046-7.

Density

The density of M&T Catalyst T-12 was determined according to the procedure described in ASTM D 891-59(C) for specific gravity at 15.56°C of industrial aromatic hydrocarbons. However, since T-12 is a solid below 19°C, the determination was made at 25°C and the specific gravity values were converted to density in conformance with the JPL Specifications format. As shown in Table VI, the value of 1.046 g/ml is in agreement with manufacturer's specification of 1.05 g/ml.

Viscosity

The viscosity of T-12, given in Table VI, was determined at 24.8°C in accordance with the procedure specified in ASTM Method D-1084(B). The sample was transferred to a 600-ml beaker, de-aerated in a vacuum oven for 1/2 hour, and conditioned at temperature for 30 minutes prior to testing.

D. RTV CURING AGENT 615B

Little information has been made available on the nature of the curing agent 615B, used with RTV-615A; however, it is known to contain a catalyst dispersed in a silicone. Since a relatively large amount of this agent is used (about 10%), determination for hydrolyzable halide was considered meaningful; the density was determined as a simple quality control procedure. Results of the determinations and the procedures used are given in Table VII.

Table VI

DETERMINATION OF CHEMICAL AND PHYSICAL PROPERTIES:
M&T CATALYST T-12 (M&T Chemical Co.)*

Property	Test Method	Values
Hydrolyzable halide	TM-5046-1†	< 0.001%
Tin Content	TM-5046-7†	18.71-18.76 wt-%
$Density_4^{25}$	ASTM D 891-59(C)	1.046-1.046 g/ml
Viscosity at 25°C (No. 1 spindle, 4 rpm)	ASTM D 1084(B); modified by GE, Spec Guide CDS-373C	40 poises

* Used for RTV-11, RTV-60, and RTV-560.

† See Section II

Table VII

DETERMINATIONS OF CHEMICAL AND PHYSICAL PROPERTIES:
RTV-615B (General Electric Company)

Property	Test Method	Values
Hydrolyzable halide	TM-5046-6*	< 0.001%
$Density_4^{25}$	ASTM D 891-59(C)	1.002-1.003 g/ml

* See Section II

II. SPECIFICATION TEST METHODS DEVELOPED AT SRI

Following the selection of properties to be determined for general classes of polymeric materials, investigations were made of available test methods which could be used directly or with some modification. It was found that ASTM methods were available for many of the selected properties and they were pressed into use wherever possible since they have been thoroughly evaluated and standardized and are already in wide use. In some instances, however, classical procedures had to be modified by appropriate selection of reagents or handling techniques; in other instances, procedures recommended by manufacturers or published in the open literature were found satisfactory.

As a result, a number of test methods have been developed and suggested for incorporation into JPL Specifications. The details of these methods are given in the following pages; method code numbers have been assigned for ease of reference.

HYDROLYZABLE HALIDE CONTENT OF EPOXY ADHESIVES

Reference: ASTM Method D 1726-62T, "Hydrolyzable Chlorine Content of Liquid Epoxy Resins"

Procedure: Prepare and hydrolyze the sample in accordance with the directions given in ASTM D 1726-62T.

Then, add 10 ml of 1:1 nitric acid solution to the hydrolyzate and dilute with an equal volume of distilled water.

Titrate the solution with 0.1 N silver nitrate solution, using a silver-mercurous sulfate reference electrode system as indicator. Plot the incremental volume of silver nitrate consumed versus the emf of the electrode system to locate the end point.

Blank determinations are to be conducted concurrently with the sample.

Calculation (assuming all halide to be chloride):

$$\% \text{ hydrolyzable halide} = \frac{(A-B) \times N \times 3.55}{W}$$

where A = ml of silver nitrate solution required to titrate the sample,

B = ml of silver nitrate solution required to titrate the blank,

N = normality of the silver nitrate solution,

and W = weight of sample in grams.

AMINE-NITROGEN CONTENT OF EPOXY CURING AGENTS

Reference: Welcher, F. J., (Ed.), Standard Methods of Chemical Analysis, D. van Nostrand Co., Inc., New York, 1963, Vol. II, Part A, p. 488.

Procedure: Weigh accurately (± 0.1 mgm) about 0.2 g of the curing agent and dissolve in 25-50 ml of glacial acetic acid.

Titrate the sample solution with 0.1 N perchloric acid solution using methyl violet indicator (0.25% in glacial acetic acid); the color change is violet to green.

Perchloric acid solution: Dissolve about 8.5 ml of 70% perchloric acid in 1 liter of glacial acetic acid; add cautiously in small portions about 15 ml of acetic anhydride; allow to stand overnight before use. Standardize against sodium acetate solution (0.53 g of dried sodium carbonate in enough glacial acetic acid to make 100 ml of solution.).

Calculation:

$$\% \text{ amine nitrogen} = \frac{V \times N \times 14.0}{W}$$

where V = ml of perchloric acid solution to titrate the sample,

N = normality of the perchloric acid solution,

and W = weight of sample in grams.

FILLER CONTENT OF EPOXY ADHESIVE, EPON 917

References: Shell Chemical Company Method ADM-3,
JPL Specification ZMF-4071-0001

Procedure: The procedure is identical to that recommended by the Shell Company and included in JPL Specifications for epoxy adhesives, with the following exception:

For Epon 917, methylethylketone is to be used in place of chlorobenzene for the extraction.

ACETONE-SOLUBLE CONTENT, EPOXY ADHESIVE TAPES

Procedure: Weight 10 g (±10 mgm) of the tape into a previously dried and weighed (±10 mgm) Soxhlet paper extraction thimble.

Extract the sample in a Soxhlet apparatus with 250 ml of acetone for 4 hours.

Dry the thimble and residue overnight at 110°C; cool in a desiccator to room temperature and re-weigh.

Calculation:

$$\% \text{ acetone soluble} = \frac{(W_o - W_f) \times 100}{W_o - W_t}$$

where W_o = original weight of thimble plus sample,

W_f = final weight of thimble plus residue,

and W_t = weight of thimble.

FILLER CONTENT OF RTV-SILICONE BASE MATERIALS

Procedure: Weigh 0.3-0.4 g (± 0.1 mgm) of the silicone base and 0.2-0.3 g (± 0.1 mgm) of Celite filter aid into a dry 150-ml beaker. Add 50 ml of chloroform and cover the beaker.

Stir the mixture in the beaker with a glass rod in order to disperse completely the insoluble matter present in the sample.

Fit an 125-ml suction flask with a rubber crucible holder and, with the aid of tongs, place a dried and weighed (± 0.1 mgm) glass funnel with a medium-porosity sintered-glass frit into the holder.

Decant the sample mixture through the funnel using suction; wash the residue out of the beaker into the funnel and wash the inner walls of the funnel with small portions of chloroform, using a total of about 20-30 ml. Release vacuum and wash the outer body and stem of the funnel with a few ml of chloroform to remove any adherent filtrate.

Dry the funnel and contents for 30 minutes at 150°C; then cool in a desiccator to room temperature and weigh to the nearest 0.1 mgm.

Calculation:

$$\% \text{ filler content} = \frac{100\ (W_t - F - C)}{W}$$

where W_t = weight of funnel plus filler plus Celite,

F = weight of funnel,

C = weight of Celite,

and W = weight of sample.

HYDROLYZABLE HALIDE CONTENT OF RTV-SILICONE BASE MATERIALS

Reference: McHard, J. A., "Silicones," in G. M. Kline, Analytical Chemistry of Polymers, Interscience Publishers, Inc., New York, 1963, Part I, p. 364.

Procedure: Weigh 5-6 g (± 10 mgm) of the silicone-base material into an 150-ml beaker.

Add 50 ml of 95% ethanol and cover the beaker with a watch glass.

Allow the mixture to stand for 10 minutes and then titrate potentiometrically with standardized 0.1 N sodium hydroxide, plotting the potential at each 0.01-ml increment.

Calculation (assuming all halide to be chloride):

$$\% \text{ hydrolyzable halide} = \frac{V \times N \times 3.55}{W}$$

where V = ml of NaOH solution used,
N = normality of NaOH solution,
and W = weight of sample in grams.

TIN CONTENT OF DIBUTYLTINDILAURATE

Reference: Gilman, H., and Rosenberg, S. D., J. Am. Chem. Soc., 75, 3592 (1953)

Procedure: Weigh 0.7 g (±1 mgm) of organotin compound into a previously ignited and weighed 30-ml porcelain crucible.

Use of a Vycor crucible will provide for visibility of the sample during decomposition.

Add 3.5 ml of concentrated sulfuric acid (sp. g. 1.84) to the sample and cover the crucible.

Heat the top of the crucible with a Bunsen burner (caution) and gradually lower the position of the flame by the sides of the crucible until the flame is directed toward the bottom. Continue heating until carbonaceous material is converted to a white solid.

Remove the crucible cover and ignite the crucible over a Bunsen burner for 0.5 hour; cool in a desiccator, and weigh.

Calculation:

$$\% \text{ tin} = \frac{\text{Wt. of } SnO_2 \times 78.77}{\text{S. Wt.}}$$

VACUUM-WEIGHT-LOSS OF POLYMERS:
PROCEDURE FOR ESTABLISHING WEIGHT-LOSS LIMITS

Thermal-vacuum apparatus: A complete description of this apparatus is given in Interim Report No. 2, this Contract.

Samples and recording: Duplicate samples are prepared for each material for weight-loss determinations to be made after 48, 96, and 192 hours of exposure to the thermal-vacuum environment of 125°C and 10^{-6} torr. By appropriate scheduling, complete data for 2 materials can be obtained in 10 days.

Identify samples as completely as possible giving all information available.

Prepare samples so as to provide maximum weight within restricting dimensions of test chambers.

Note sample dimensions, number of pieces, and method of preparation (cutting, sawing, coiling of films, etc.) and time and temperature for cure or postcure (if required).

Humidify samples at least 24 hours in a 50%-constant-humidity-chamber at least 24 hours prior to initial weighing.

Record sample weight data in the following fashion:

Initial	After ___ hours
Wt. of sample + holder	Initial Wt. of sample + holder
Wt. of holder	Final wt. of sample + holder
Wt. of sample	Weight lost

Calculate %-weight-loss for each time-interval.

System operation: Wax baths are maintained constantly at 125°C ± 2. At the termination of each run (2 materials), the sample chambers and stopcocks are cleaned with "Trisol" (1:1:1 methanol, chloroform, and benzene) and evacuated; at this

35

time, liquid nitrogen traps are removed and the residual gases are pumped out.

Insert samples in chambers and immediately open large stopcocks slowly to evacuate sample chambers.

Start timing when pressure in the sample chambers is again at 10^{-3} torr; fill liquid nitrogen traps.

At termination of prescribed time at temperature and vacuum: Close off large stopcock and vent sample chamber through small stopcock.

Carefully remove cap assembly with suspended sample, immediately place sample in desiccator, and place desiccator in balance room. After exactly 1/2 hour, weigh sample.

MICRO-VCM DETERMINATIONS:
VCM AND WEIGHT LOSS AT 125°C AND 10^{-6} TORR
(VCM Collector Plates at 25°C)

Micro-VCM apparatus: A complete description of this apparatus is given in Interim Report No. 2, this Contract.

Samples and recording: Identify samples as completely as possible giving all information available.

Prepare samples according to manufacturer's instructions for curing or postcuring, or use "as received." Make complete notes of procedures used for preparing and curing samples.

Procedure: Place samples of about 200 milligrams, cut into small pieces, into weighed aluminum boats (generally used for micro-combustion analyses) and condition in a 50% humidity-atmosphere for at least 24 hours prior to weighing.

Weigh the samples on a microbalance. Weigh the polished and cleaned copper collector plates on a microbalance.

Place the samples (in the aluminum boats) in the sample compartments of the micro-VCM apparatus and note the location. Affix the weighed collector plates to the apparatus and note the location in reference to specific samples.

When samples and collector plates are in position, cover the apparatus with the bell-jar and begin evacuation; at 10^{-3} torr, activate the liquid nitrogen trap and the cooling system for the collector plates. When the system is at least 10^{-5} torr, elevate the temperature of the copper blocks containing the samples to 125°C.

After the samples have been maintained at 125°C for 24 hours, allow the system to cool, in vacuo, to a temperature of at least 50°C. Then vent the system with dry nitrogen or helium.

Remove the samples and collector plates in a systematic order and store in appropriate desiccators.

Begin weighing of samples after 1/2 hour of storage in the desiccator, in the order of their removal from the thermal-vacuum system. Then weigh the collector plates.

Data to be reported are: sample weight in grams, sample weight-loss in wt-%, and VCM in wt-%.

III. THERMAL-VACUUM WEIGHT-LOSS DETERMINATIONS

A standardized vacuum weight-loss apparatus and procedure have been developed for evaluation of candidate polymeric materials for use in spacecrafts. Details of the apparatus, establishment of the procedure, and a discussion of specific determinations are included in this Section, as well as a summary of the weight-loss limits determined for the more promising candidate materials for Specifications. Directions for performing the vacuum-weight-loss determinations are given in Section II, TM-5046-8.

A. VACUUM-WEIGHT-LOSS APPARATUS

The vacuum-weight-loss apparatus is shown in the photograph in Figure 5. A design drawing, including the parts list, is given in Figure 6 so that the appatus may be readily duplicated.

As shown in Figures 5 and 6, the apparatus accommodates duplicate samples under identical vacuum-thermal conditions; the large-bore stopcocks ensure maximum rate of evacuation on each sample and valid pressure measurements (made via a gage directly above the sample chamber).

The purpose of the well near the joint of each sample chamber is to collect substances which may condense at cooler temperatures and to prevent re-deposit of these substances on the samples. One-mm stopcocks are affixed to the arms leading from the sample chambers to permit venting at termination of the tests.

Glass hooks have been attached to the caps of each chamber so that samples may be suspended directly by wires or in glass containers. (In view of the anticipated reactivity of some polymeric materials with wire material, Nichrome wires have been gold-plated in order to provide an inert contact surface; platinum wire, of sufficient strengh, could also be used.)

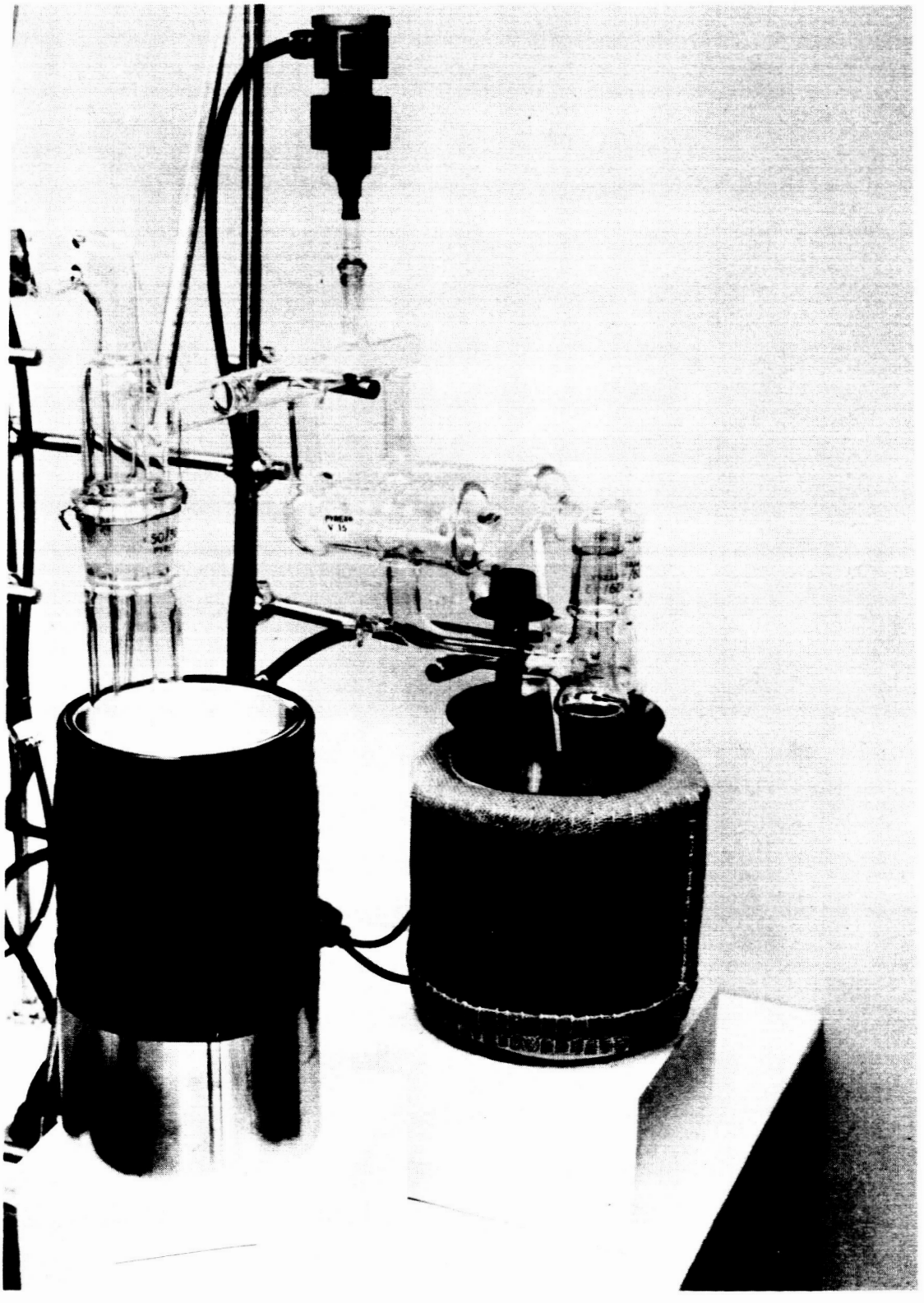

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FIG. 5 PHOTOGRAPH OF VACUUM-WEIGHT-LOSS APPARATUS

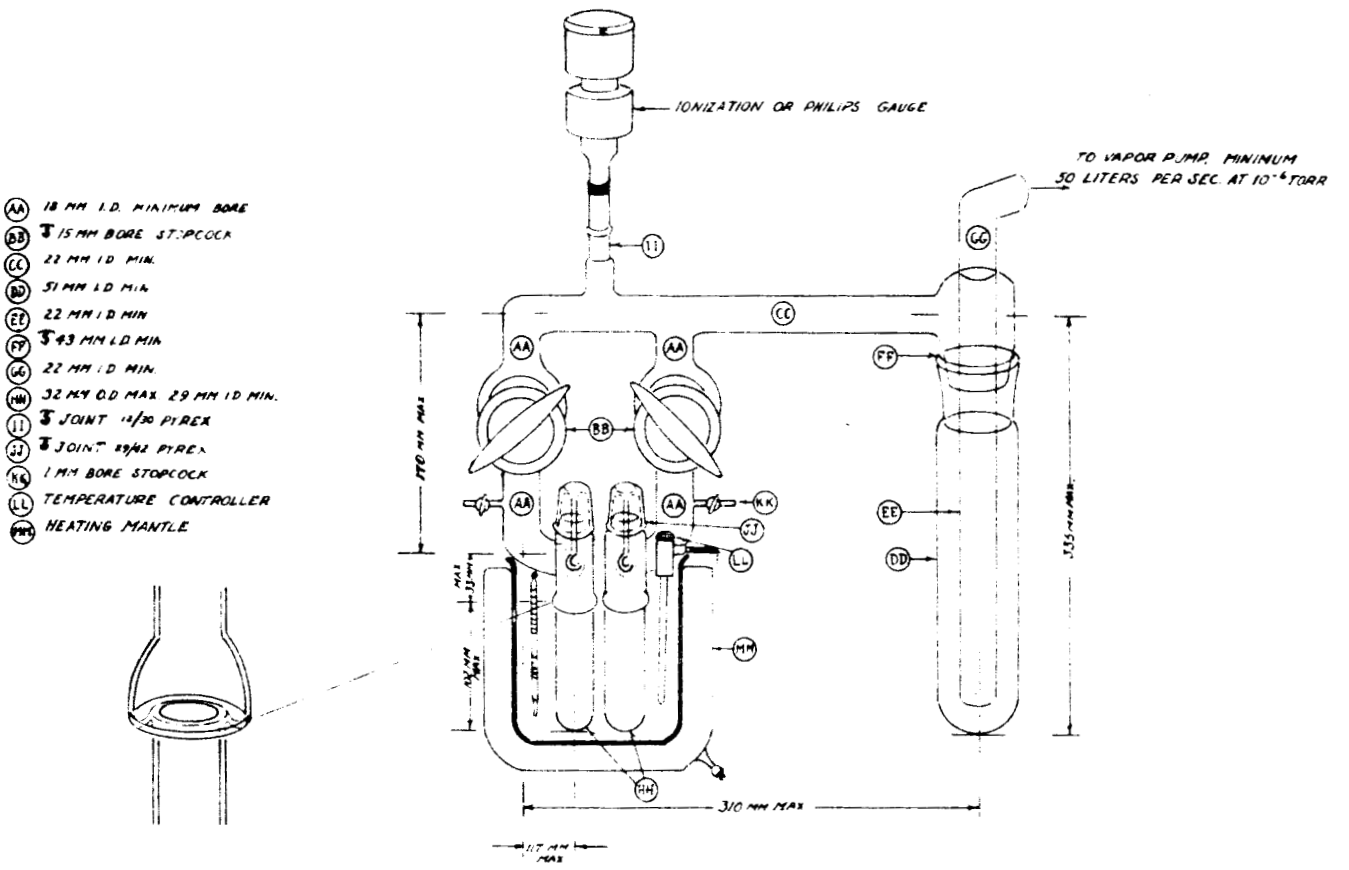

FIG. 6 DESIGN DRAWING OF VACUUM-WEIGHT-LOSS APPARATUS

A good grade of high-temperature vacuum grease is used in order to obviate difficulties created by channeling or outgassing (silicones); "Apiezon-T" or equivalent has been found satisfactory.

The sample chambers are immersed in Fisher bath wax contained in stainless beakers fitted with heating mantles; temperature is maintained by a thermoregulator-variable transformer system. The input to the heating mantles is adjusted so that the wax temperature is maintained at 125°C with only minimal control afforded by the thermoregulator; this temperature has been selected since prior work has shown that most polymeric materials do not undergo decomposition at 125°C.

B. VACUUM AND CONTROL SYSTEM

Each vacuum-weight-loss apparatus is attached to a primary manifold leading directly to the pumping system. Figure 7 illustrates a vacuum system consisting of four pumping stations of the kind shown in Figure 5. This arrangement has been set up in order to facilitate the generation of copious data for determining parameters which eventually will be used to establish materials specifications limits. The primary manifold has sufficient pumping speed to accommodate the four units. The primary manifold is a 6-inch glass pipe leading to the fore pump via a water-cooled baffle and a 6-inch diffusion pump. Specifications for this vacuum and control system which will accommodate four vacuum-weight-loss apparatuses are as follows:

Fore pump: 0.5 liters/second at 10^{-3} torr
Diffusion pump: 1400 liters/second at 10^{-5} torr
Water-cooled baffle: Chevron-ring type
Vacuum gages: 0.25 to 1 x 10^{-7} torr
Temperature controller: 95 to 200 ± 2°C
Heating mantles: 95 to 200°C

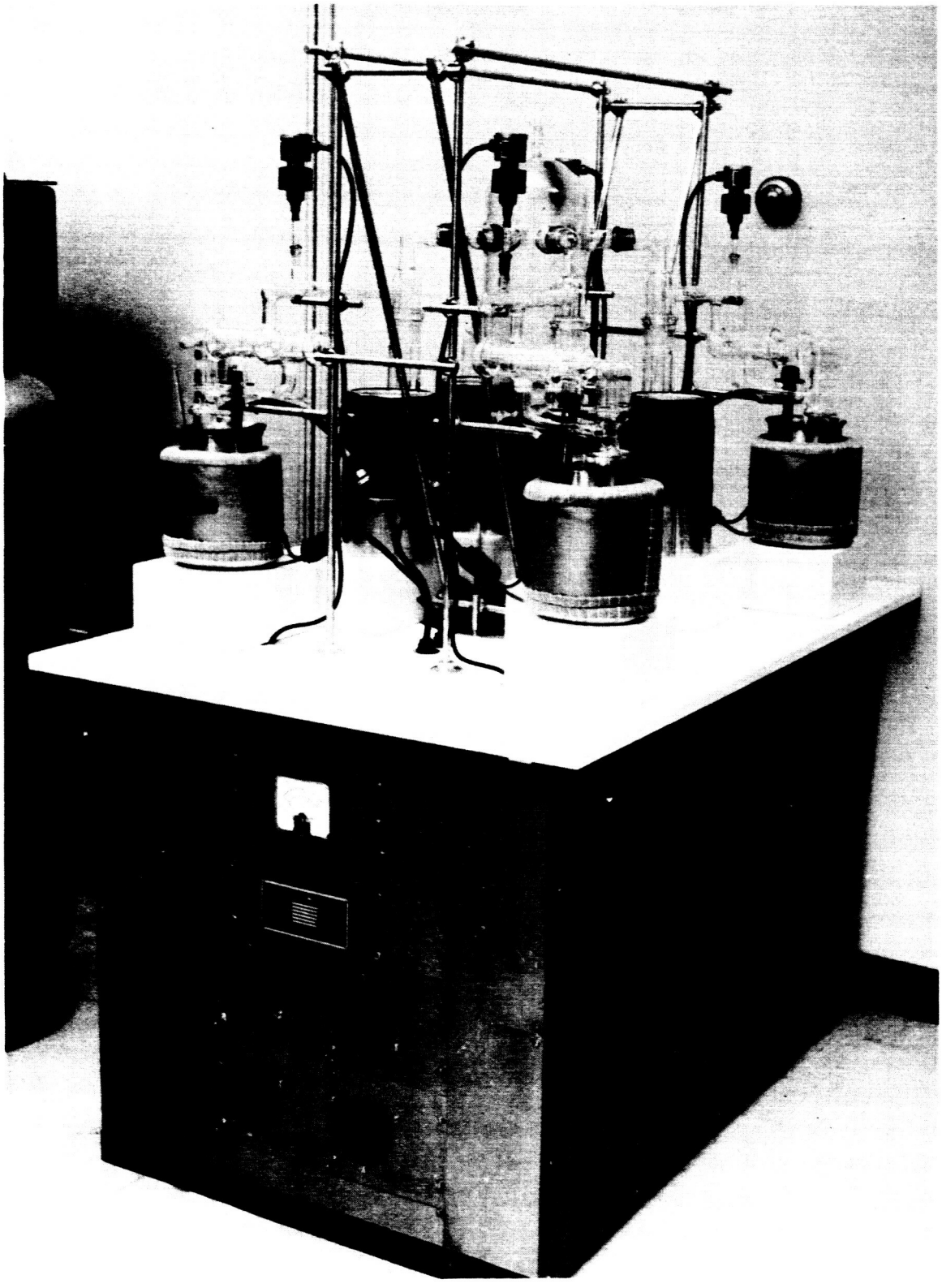

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FIG. 7 VACUUM SYSTEM WITH VACUUM-WEIGHT-LOSS APPARATUS

C. PROCEDURE

Development of the parameters for a standardized procedure for vacuum-weight-loss limits has involved investigation of sample preparation, weighing techniques, and time functions. Two materials, well-characterized in prior work,[1] have been selected as control samples for not only vacuum-weight-loss work but also for other screening procedures; these are General Electric silicone elastomers SE-555 (white) and SE-555 (gray).

Sample Conditioning and Sample Weights

Since the initial weight of polymeric samples is dependent on ambient conditions (surface adsorption of atmospheric moisture and gases), a standardized conditioning procedure has been adopted for ensuring reproducibility of results in any climate; samples are placed in a 50%-relative-humidity environment at 20-30°C for at least 24 hours prior to initial weighing.

> A 50%-constant-humidity environment is easily maintained by confining a saturated solution of $Ca(NO_3)_2 \cdot 4H_2O$.

It is general knowledge that polymeric samples will adsorb moisture and air, even in a desiccator, after exposure to a thermal-vacuum environment. Therefore, sufficient time must be allowed to permit exposed samples to reach an equilibrium temperature in the balance room and an optimum time must be selected for weighing back the samples. In view of the change in weight with time, illustrated below, an exact time for weighing samples after thermal-vacuum exposure is prescribed for specifications purposes; exactly one-half hour has been selected to provide maximum cooling and minimum weight increase:

Time lapse after removing samples from vacuum-thermal environment and storing in desiccator (SE-555-white)	Sample Wt., g
15 minutes	5.2159
30 minutes	5.2163
24 hours	5.2171

Sample Configuration

In an attempt to determine the effect of sample size and configuration, SE-555 (white) was prepared in three different ways:

(1) As received, 3 strips of 2" × 1/2" × 1/16";

(2) As received, sliced with scalpel into pieces of about 1/2" × 1/16" × 1/64";

(3) As received, frozen with liquid nitrogen and ground in a mortar; dried under low vacuum at room temperature for 1/2 hour, and stored in a desiccator until initial weighing.

The samples were exposed to the thermal-vacuum environment for periods of 24, 72, and 96 hours in order to remain within the bounds of a normal working week. The results of these determinations, shown below in order, indicate that the more tedious methods of preparation provide little gain over the results obtained from simple preparation:

(1) 0.46% wt-loss at 24 hr, 0.44% at 96 hr,

(2) 0.40% wt-loss at 24 hr, 0.46% at 96 hr,

(3) 0.35% wt-loss at 24 hr, 0.56% at 96 hr.

The results obtained from prior mass spectrometric work were a little higher for a longer exposure period, i.e., 0.65% at 144 hours. However, all results are within a reasonable range for specifications purposes (0.45-0.65%), and those obtained with the standardized apparatus are quite adequate for control limits.

D. DISCUSSION OF WEIGHT-LOSS DETERMINATIONS

RTV-Silicone Potting Compounds

The weight-loss determinations for a series of cured RTV-silicone potting compounds (supplied by the General Electric Company) indicated that excessive amounts of material were given off at 125°C *in vacuo*; the results for RTV-11, -60, -560, and -615 ranged from 1-4% after 192 hours of exposure. Since prior work[1] has shown that a substantial portion of the material released by silicone polymers in a thermal-vacuum environment is attributable to unpolymerized starting material (diols) as well as low-molecular-weight silicone oil and other additives, it seemed appropriate to subject these cured polymers to a postcure, of the specific kind recommended by the manufacturer for thick sections of materials. The materials were postcured for 24 hours at 150°C; weight losses incurred during postcuring were as follows:

RTV-11	0.12
RTV-60	0.09
RTV-560	0.33
RTV-615	0.05

The vacuum-weight-losses of the postcured RTV compounds are compared with those obtained for the originally-cured samples in Table VIII; a study of the data in this Table shows that postcuring has a noticeable effect on the vacuum-weight-loss of the RTV compounds and indicates clearly that the postcuring treatment increases the degree of polymerization.

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[1]Muraca, R. F., *et al.*, "Space Environment Effects on Polymeric Materials," Stanford Research Institute, *Final Report*, *Project 4257*, December 1963.

Silicone Elastomers

Weight-loss data for General Electric silicone elastomers SE-555 (white) and SE-555 (gray) are summarized in Table IX. Comparison with data previously acquired in mass spectrometric work indicates that the standardized vacuum-weight-loss system is providing nearly-maximum results:

SE-555 (white)	0.44% at 96 hr (Std.) 0.65% at 144 hr (M.S.)
SE-555 (gray)	0.74% at 192 hr (Std.) 0.78% at 164 hr (M.S.).

Also included in Table IX are results for General Electric silicone elastomers SE-3604, SE-3613, and SE-3713. The -3613 and -3713 were postcured (at GE) for 24 hours at 250°C, and required no special treatment. In fact, these materials display a definite superiority in respect to weight-loss criteria. They were examined in view of their good performance in mechanical-property tests (see Section IV).

All of the silicone elastomers mentioned are included in the summary of weight-loss limits for selected polymers, given in Table VI.

Polycarbonate Plastics

In an effort to correlate loss of material with the unfavorable results obtained in thermal-vacuum mechanical-properties tests (Phase II) of a Lexan film, weight-loss determinations were made for two similar General Electric Lexan chips; unfortunately, the grade and code number of the film sample has not yet been identified, but the chips are graded as medium viscosity 101-111 (heat-stabilized) and 101-112 (tinted). As shown in Table X, by weight-loss criteria, these formulations would be considered suitable for spacecraft use.

The leveling-off of weight loss within the 48 hour period might indicate that the released material is probably quite volatile; this is corroborated by mass spectral identification (see Section VI).

Epoxy Coating Materials

Samples of epoxy coating materials were prepared for vacuum-weight-loss determinations in the following fashion:

> The coatings were applied to copper-wire coils of suitable size to fit in the sample chambers; three-foot lengths of 16-gage copper wire were wound on a half-inch mandrel. The copper coils were removed from the mandrel and in the coating material, drained, and cured; then, a second coat was applied, if required, and treated in the same fashion.

Eccocoat EC/200, supplied by Emerson and Cuming, Inc., was cured for 6 hours at room temperature and 2 hours at 120°C (2 coats); Eccocoat VE was cured for 6 hours at room temperature and 2 hours at 95°C (1 coat). Vacuum-weight-loss results for these coatings are given in Table XIII. As indicated, the weight losses for both materials are far in excess of acceptable limits and no indication of leveling-off is given after 192 hours of exposure in the thermal-vacuum environment. Evidence observed thus far indicates that these resins require more extended curing at elevated temperatures, that they undergo slow decomposition in the thermal-vacuum environment, or that the curing cycle is not long enough to remove any solvents that are present.

Weight-loss data were also obtained for a modified-epoxy coating material, Clear Varnish B-276, supplied by Westinghouse Electric Corporation. Samples were applied to copper coils as described above and cured for 4 hours at room temperature, followed by 1 hour at 165°C, in accordance to manufacturer's instructions. As shown in Table XI, the weight loss apparently levels off in 96 hours, but nevertheless is well outside of acceptable limits. Therefore, the curing time for this material was extended to 16 hours at 165°C, and a much lower weight loss was observed, i.e., 0.56% compared to 2.4% (see Table XI).

Epoxy-Silver Solder Paste

Samples of a silver-filled epoxy-paste solder, Eccobond Solder 56C (supplied by Emerson and Cuming, Inc.) were prepared by using both a catalyst for moderate temperature properties, #9, and for improved high-temperature properties, #11, and were applied to copper coils for the weight-loss determinations. Solder 56C/9 was cured for 2 hours at 50°C and 56C/11 was cured for 4 hours at 65°C; in both instances, weight-loss levels were established within 48 hours, indicating that the values of about 0.7% and 1.3%, respectively, might be attributable simply to nonremoval of solvents during the cure. Since this is a unique and important material, new samples were prepared for 48-hour determinations by extending the curing time (at the prescribed temperature) to 16 hours, i.e., overnight. As shown in Table XII, the weight loss for 56C/9 was cut in half, and that for 56C/11 was reduced by a factor of five.

Polyurethane Conformal Coatings

The JPL Conformal Coatings-1001 and -1002, packaged in plastic syringes as frozen adhesives, were stored at -40°F according to manufacturer's instructions (Ablestik Adhesive Company) since they have a shelf-life of only 24 hours at room temperatures. Formulation of the two materials is the same except that JPL-1001 contains a fluorescent dye; preparation of samples for weight-loss determinations were carried out as follows:

> The syringe and contents were warmed to room temperature, and the adhesive was released from the barrel of the syringe onto a glass plate. The plate with the adhesive was placed in an oven maintained at 75°C for the recommended curing period of 4 hours.
>
> The plate and cured coating were then cooled to room temperature, and the coating was released with the aid of a stainless steel spatula.

The resultant coatings were transparent, somewhat tacky, and quite tough. Average thicknesses were as follows: JPL-1001, 0.050"; JPL-1002, 0.065".

The results of the weight-loss determinations are summarized in Table XIV. The values for JPL-1002 appear slightly better than JPL-1001 after 192 hours of exposure in the thermal-vacuum environment; however, the latter achieved an apparent leveling-off within 96 hours, and the former does not show such an indication after 192 hours.

Acrylic-Glass Fiber Sleeving

Weight-loss determinations were made for two acrylic-resin treated glass-fiber sleeving materials used for wire and cable insulation, Ben Har Acryl C-2 and Ben Har Acryl A (Grad BAI) supplied by the Bentley-Harris Manufacturing Company. The results of these determinations are summarized in Table XV; at this time, Ben Har Acryl A is considered unsuitable in view of the white, powdery coating (not identified) which began depositing on the walls of the sample chambers within one-half hour of exposure to the thermal-vacuum environment.

Table VIII

THERMAL-VACUUM WEIGHT-LOSS DETERMINATIONS:
GENERAL ELECTRIC SILICONE POTTING COMPOUNDS

125 °C and 10^{-6} torr

Material	Treatment	S. Wt. av, g	Weight Loss av., %		
			48 hr	96 hr	192 hr
RTV-11	as received	3.0	1.33		
		3.0		1.57	
		3.0			1.68
RTV-11	postcured 24 hr at 150°C	3.0		0.48	
		3.0			0.72
RTV-60	as received	3.9	1.03		
		3.9		1.01	
		3.9			0.95
RTV-60	postcured 24 hr at 150°C	3.9		0.45	
		3.9			0.51
RTV-560	as received	4.0	3.43		
		3.7		3.83	
		3.9			3.85
RTV-560	postcured 24 hr at 150°C	3.5		0.67	
		3.5			0.77
RTV-615	as received	2.5	1.47		
		2.6		1.64	
		2.7			1.77
RTV-615	postcured 24 hr at 150°C	2.4		0.97	
		2.7			1.02

Table IX

THERMAL-VACUUM WEIGHT-LOSS DETERMINATIONS:
GENERAL ELECTRIC SILICONE ELASTOMERS

(125°C and 10^{-6} torr)

Material	Treatment	S. Wt. (av), g	Weight Loss (av), %		
			48 hr	96 hr	192 hr
SE-555 white	as received	2.3	0.41		
		2.4		0.44	
SE-555 gray	as received	1.6	0.42		
		1.6		0.65	
		1.6			0.74
SE-3613 24 480	postcured at GE	3.5	0.09		
		3.6		0.10	
		3.5			0.10
SE-3604	as received	3.0	0.08		
		3.1		0.17	
		3.1			0.15
SE-3713 24 480	postcured at GE	3.1	0.19		
		3.2		0.20	
		3.2			0.19

Table X

THERMAL-VACUUM WEIGHT-LOSS DETERMINATIONS:
GENERAL ELECTRIC POLYCARBONATE PLASTICS

(125°C and 10^{-6} torr)

Material	Treatment	S. Wt. (av), g	Weight Loss (av), %		
			48 hr	96 hr	192 hr
Lexan 101-111	as received	1.8	0.22		
		1.9		0.20	
		1.8			0.20
Lexan 101-112	as received	1.8	0.22		
		1.8		0.20	
		1.7			0.19

Table XI

THERMAL-VACUUM WEIGHT-LOSS DETERMINATIONS:
WESTINGHOUSE EPOXY MATERIALS

(125 °C and 10^{-6} torr)

Material	Treatment	S. Wt. av, g	Weight Loss (av), %		
			48 hr	96 hr	192 hr
Clear Varnish B-276	cured 1 hr at 165 °C	0.8 0.8 0.8	2.38	2.64	2.58
Clear Varnish B-276	cured 16 hr at 165 °C	0.8	0.56		
Micarta H-8457 Circuit Board	as received	2.8 2.8 2.7	0.33	0.40	0.38
Micarta 65M25 Circuit Board	as received	3.0 2.6 3.1	0.36	0.38	0.41

Table XII

THERMAL-VACUUM WEIGHT-LOSS DETERMINATIONS:
EMERSON AND CUMING EPOXY-SILVER SOLDER PASTES

125 °C and 10^{-6} torr

Material	Treatment	S. Wt. av, g	Weight Loss (av), %		
			48 hr	96 hr	192 hr
Eccobond Solder 56C/9	cured 2 hr at 50 °C	1.5 1.3 1.6	0.63	0.87	0.71
	cured 16 hr at 50 °C	1.5	0.31		
Eccobond Solder 56C/11	cured 4 hr at 65 °C	1.5 1.6 1.9	1.12	1.44	1.26
	cured 16 hr at 65 °C	2.7	0.22		

Table XIII

THERMAL-VACUUM WEIGHT-LOSS DETERMINATIONS:
EMERSON AND CUMING EPOXIDE COATINGS

(125 °C and 10^{-6} torr)

Material	Treatment	S. Wt. (av), g	Weight Loss (av), %		
			48 hr	96 hr	192 hr
Eccocoat EC/200	cured 6 hr at ambient and 2 hr at 120 °C	0.7 0.7 0.6	3.02	3.48	5.82
Eccocoat VE	cured 6 hr at ambient and 2 hr at 95 °C	1.5 1.3 1.0	2.71	6.23	8.98

Table XIV

THERMAL-VACUUM WEIGHT-LOSS DETERMINATIONS:
POLYURETHANE CONFORMAL COATINGS, ABLESTIK ADHESIVE COMPANY

(125 °C and 10^{-6} torr)

Material	Treatment	S. Wt. (av), g	Weight Loss (av), %		
			48 hr	96 hr	192 hr
JPL-1001	cured 4 hr at 75 °C	1.7 1.9 2.1	0.37	0.53	0.54
JPL-1002	cured 4 hr at 75 °C	2.2 2.3 2.4	0.29	0.30	0.38

Table XV

THERMAL-VACUUM WEIGHT-LOSS DETERMINATIONS:
ACRYLIC-GLASS FIBER SLEEVING, BENTLEY-HARRIS MFG. COMPANY

(125 °C and 10^{-6} torr)

Material	Treatment	S. Wt. (av), g	Weight Loss (av), %		
			48 hr	96 hr	192 hr
Ben Har Acryl A* (Grade BAI)	as received	2.5 2.6 2.5	0.32	0.39	0.43
Ben Har Acryl C-2	as received	2.3 2.3 2.2	0.25	0.27	0.34

* deposited powdery white film (unidentified) on walls of sample chamber

E. SUGGESTIONS FOR WEIGHT-LOSS LIMITS

Suggestions for weight-loss limits for representative polymeric materials are made subsequent to a study of the results obtained after exposure of fresh, duplicate samples for periods of 48, 96, and 192 hours in the standardized vacuum-weight-loss apparatus. The primary intent of the periodic determinations is to discern the maximum amount of weight-loss incurred in the least amount of time, that is, the time at which weight-loss appears to level off. Since the majority of polymeric materials considered for use in spacecrafts do not decompose in the thermal-vacuum environment of 125°C and 10^{-6} torr, the weight-loss can be attributed generally to release of volatile materials such as solvents and occluded moisture and gases, but sometimes to unpolymerized starting materials, processing oils, etc.

Correlative studies have shown that the weight-loss which is immediate and thereafter steady is due largely to extraneous materials, such as solvents, which will not affect the mechanical properties of the materials; very often, a simple postcure will alleviate this situation. On the other hand, the materials which incur increasing amounts of weight-loss are suspect when one considers the effect on mechanical properties. If more than 1% of weight-loss is incurred, a material is generally not recommended since the consensus is that weight-losses greater than 1% may contribute to the degradation of mechanical properties. Therefore, weight-loss limits for specific exposure times are suggested in Table XVI for materials which may be considered as candidates for spacecraft use; the time is selected according to the results which indicate that a steady-state weight-loss has been incurred in less than 200 hours.

Table XVI

SUMMARY OF DETERMINED WEIGHT LOSS LIMITS FOR SELECTED POLYMERIC MATERIALS

125°C and 10^{-6} torr

Material	Mfr.*	Treatment	Wt. Loss, %
Silicones, potting compounds			
RTV-11	GE	postcure 24 hr at 150°C	0.60 ± 0.1 at 96 hr
RTV-60	GE	postcure 24 hr at 150°C	0.15 ± 0.05 at 96 hr
RTV-560	GE	postcure 24 hr at 150°C	0.72 ± 0.1 at 96 hr
Silicones, elastomers			
SE-555 white	GE	as received	0.50 ± 0.05 at 96 hr
SE-555 gray	GE	as received	0.70 ± 0.05 at 168 hr
SE-3604	GE	as received	0.17 ± 0.05 at 48 hr
SE-3613	GE	postcured 24 hr at 250°C	0.10 ± 0.05 at 48 hr
SE-3713	GE	postcured 24 hr at 250°C	0.20 ± 0.05 at 48 hr
Epoxy, coating			
Clear Varnish B-276	We	cure 4 hr at 25°C plus 16 hr at 165°C	0.56 ± 0.05 at 48 hr
Epoxy-silver solder paste			
Eccobond 56C 9	El	cure 16 hr at 70°C	0.31 ± 0.05 at 48 hr
Eccobond 56C 11		cure 16 hr at 65°C	0.22 ± 0.05 at 48 hr
Epoxy-fiber glass circuit boards			
Micarta B-8457	We	as received	0.40 ± 0.05 at 96 hr
Micarta 65M25	We	as received	0.40 ± 0.05 at 96 hr
Polyurethanes, conformal coating			
JPL-1001	Ab	cure 1 hr at 75°C	0.53 ± 0.05 at 96 hr
JPL-1002	Ab	cure 1 hr at 75°C	0.35 ± 0.05 at 96 hr
Acrylic-glass fiber, sleeving			
Ben Har Acryl C-2	B-H	as received	0.30 ± 0.05 at 48 hr
Polycarbonates, structural plastics			
Lexan 101-111	GE	as received	0.20 ± 0.05 at 48 hr
Lexan 101-112	GE	as received	0.20 ± 0.05 at 48 hr

* Ab, Ablestik Adhesive Company
B-H, Bentley-Harris Mfg. Company
E-C, Emerson and Cuming, Inc.
GE, General Electric Company
We, Westinghouse Electric Corporation

PHASE II

ENGINEERING INFORMATION

IV. MECHANICAL PROPERTIES

A. MECHANICAL-PROPERTY BEHAVIOR OF POLYMERIC MATERIALS IN THE THERMAL-VACUUM ENVIRONMENT

The effects of the thermal-vacuum environment on the mechanical properties of polymeric materials were studied as a continuation of work previously described;[2] the tests performed included:

(1) Continuous and intermittent stress-relaxation tests of elastomeric materials *in situ* in the thermal-vacuum environment;

(2) Continuous and intermittent stress-relaxation tests of elastomeric materials at elevated temperatures in air;

(3) Constant load tests of plastic materials *in situ* in the thermal-vacuum environment;

(4) Constant strain rate tests of control specimens and specimens stored in the thermal-vacuum environment (elastomeric and plastic materials).

The materials studied during this period include:

Silicone rubbers SE-555, -3004, -3613, and -3713 (General Electric)
Hycar rubbers 520-67-108-1, -3 (Goodrich)
Lexan, film (annealed 1 hour at 150°C) (General Electric)

The materials currently being tested include:

Silicone rubber SE-3813
Hycar rubber 520-67-108-2
Enjay Butyl EX-1090, -1091, -1092 (postcured 4 hours at 150°C) (Enjay Chemical Company)
Polyphenylene oxide, film (annealed 1/2 hour at 180°C) (General Electric)

Test Results

In situ continuous and intermittent stress relaxation tests of rings of silicone rubbers SE-555, -3604, -3613, and -3713 and Hycar rubbers 520-67-108-1 and -3 were conducted in duplicate. Constant load tests *in vacuo* of Lexan polycarbonate film were also undertaken. Specimens of each of the materials were also stored, under no-load conditions within the vacuum-chamber at the test temperature (125°C), for later constant-strain-rate tests. Prior to raising the temperature in the test areas to 125°C, specimens were conditioned under vacuum at 50°C for periods ranging from 145 to 280 hours. Continuous and intermittent stress relaxation tests of silicone rubbers SE-555 and -3604 were also conducted at 125°C in an air environment.

Results of stress relaxation tests are presented in Figures 8 to 13, inclusive, and in Table XVII and XVIII. The effects of the vacuum thermal environment on the tensile properties of stored materials are shown in Tables XIX and XX. Environmental conditions for each test are indicated in the footnotes to the tables.

Discussion of Results

As discussed previously,[2] the results of continuous-and intermittent-stress-relaxation tests can be interpreted to yield information concerning the rates of aggregative and disaggregative reactions occurring upon degradation of rubbery materials. The decay of stress in rubbers maintained at a constant extension is a direct measure of chain-scission, or disaggregative reactions; the net effect of cross-linking (aggregative) and scission reactions is measured by the results of the intermittent test. In the latter test, if the cross-linking reactions are faster than scission, intermittently measured values of stress increase; conversely, if cross-linking is slower than scission, stress decreases.

The intermittent test yields stress values which can also be used as a measure of modulus change with time. Thus, the last datum point obtained from the intermittent test should be comparable with the value

of stress at a strain of 0.25 obtained from the constant-strain-rate test of unstrained rings stored in the vacuum-thermal environment. Another way of evaluating the data from the stress-relaxation tests is to consider how the elastomer is to be used in the spacecraft. The results of the continuous tests are directly related to an application of the elastomer where the material is under constant strain. If the material is normally relaxed or under slight compression (as in an O-ring application), the intermittent tests, or the effects of storage on tensile properties, are more directly applicable.

Examination of the results of Figures 8 and 9 and Table XVII leads to the observation that Hycar-1 is apparently more stable than Hycar-3 in the vacuum-thermal environment, although the results of the intermittent tests indicate a higher rate of cross-linking. The influence of the vacuum-thermal environment on tensile properties (Table XX) again shows that the modulus increase is greater for Hycar-1 than for Hycar-3, but the effect is small; rupture properties of the two exposed materials are not significantly different. Thus, Hycar-1 would be expected to perform better than Hycar-3, unless the materials were used in an unstrained condition; in such a case, the Hycar-3 might have slightly better characteristics.

Of the silicone elastomers, SE-555 (Figure 10) is significantly inferior to the other three materials studied (Figures 11-13, inclusive) with the results of continuous and intermittent tests indicating higher rates of degradation. The SE-555 was also shown to be definitely inferior to SE-3604 in regard to thermal stability in air (Table XVIII). In comparison with Hycar-1, however, SE-555 has superior properties. It is interesting to note at this time that both SE-555 and Hycar-1 are apparently more stable than the materials reported previously,[2] namely the Vitons, Nordels, and Hypalons. These statements are general reflections of over-all changes; consideration of material application, i.e., strained or unstrained, might re-order the relative performance expected.

By examining the test results for SE-3604, -3613, -3713 (Figures 11-13, and Tables XVII and XX), it is observed that SE-3604 is apparently the most stable, although the differences are not great. The difference between results of the stress-relaxation tests of SE-3604 and those for SE-3613 is almost insignificant; however, examination of the tensile properties (Table XX) indicates that the rupture properties of SE-3604 are almost unaffected while those of SE-3613 show significant reduction of both stress and strain at rupture. The intermittent test results for SE-3713 indicate higher stress levels; this effect is expected since the same rate of cross-linking would be reflected by higher stress levels in materials with higher concentrations of reinforcing solids. The effect of the vacuum-thermal environment on the tensile properties is approximately the same for both SE-3613 and SE-3713.

The effect of the vacuum-thermal environment on the properties of Lexan is shown in Table XIX. The major effect noted is the elimination of yielding. Rupture of the exposed material was found to occur at approximately the same stress as the yield stress of the unexposed specimens, and there was an indication that the tensile modulus may have been somewhat decreased. Constant load data are not reported because of erratic results and the extensive deformation which occurred. The distortion temperature of Lexan is reported to be about 125°C, and occasional brief excursions of storage temperature to 128-130°C resulted in step-changes in deformation of as much as 30%. These results demonstrate the unsuitability of Lexan as a structural material for use at 125°C or above. Table XIX also shows the tensile properties determined for polyphenylene oxide; this material ruptures at its maximum stress and does not yield in the manner of Lexan at the test rate and temperature used. Rupture stress is almost twice that of Lexan and the rupture strain is about the same as the Lexan yield strain.

Tests in Progress

Tests of mechanical behavior in the vacuum-thermal environment are in progress with various materials in storage as well as active tests of Hycar 520-67-108-2, SE-3813, and polyphenylene oxide film. The materials in storage include specimens of these three materials as well as rings of three batches of Enjay Butyl rubber, as noted above. Preliminary examination of results of the tests thus far indicate that Hycar-2 appears to be cross-linking at a higher rate than either Hycar-1 or -3, and that SE-3813 appears to be behaving as did SE-3713 with increased stresses being developed due to higher filler concentration. The PPO specimens are being subjected to a constant load of 2,000 psi; after 500 hours in vacuum at 125°C, one of four specimens has broken and almost no deformation has occurred in the surviving specimens.

Table XVII

EFFECT OF VACUUM-THERMAL ENVIRONMENT
ON STRESS-RELAXATION BEHAVIOR
OF HYCAR AND SILICONE RUBBERS

Material	Intermittent			Continuous		
	Approx. Time to $f(t)/f(o) > 1.0$, hours	$f(t)/f(o)$ at 20 hrs	$f(t)/f(o)$ at 500 hrs	Approx. Time to $f(t)/f(o) = 0.9$, hours	$f(t)/f(o)$ at 20 hrs	$f(t)/f(o)$ at 500 hrs
Hycar-1	1	1.16	~1.65	0.6	0.84	0.80
Hycar-3	3	1.06	1.38	0.3	0.59	0.48
SE-555 Red	2	1.06	1.36	4	0.87	0.82
SE-3604	2	1.04	1.21	220	0.92	0.89
SE-3613	3	1.08	1.32	300	0.95	0.89
SE-3713	3	1.12	1.58	125	0.94	0.86

Notes:
1. All tests conducted at strains of approximately 0.25
2. Data obtained from best curves drawn through duplicate test results
3. Exposure conditions consisted on two stages:
   Hycar-1 and -3--(a) 215 hours at 50°C and an average pressure of about 4×10^{-6} torr, (b) 1055 hours at 125°C and an average pressure of about 4×10^{-6} torr.

   SE-555 and -3604--(a) 280 hours at 50°C and an average pressure of about 4×10^{-6} torr, (b) 1040 hours at 125°C and average pressures of from 3.2 to 4×10^{-6} torr.

   SE-3613 and -3713--(a) 145 hours at 50°C and an average pressure of about 5×10^{-6} torr, (b) 910 hours at 125°C and an average pressure of about 2×10^{-6} torr.

Table XVIII

EFFECT OF AIR-THERMAL ENVIRONMENT
ON STRESS-RELAXATION BEHAVIOR OF SILICONE RUBBERS

Material	Intermittent		Continuous	
	Approx. Time to $f_t/f_o = 1.0$, hours	f_t/f_o at 90 hours	Approx. Time to $f_t/f_o = 0.8$, hours	f_t/f_o at 20 hours
SE-555 Red	> 91	1.0	27	0.81
SE-3604	>118	1.0	>118	0.92

Notes:
1. All tests conducted at strains of approximately 0.25.
2. Data obtained from tests of single specimens.
3. Environment consisted of one atmosphere of air at 125 °C

Table XIX

TENSILE PROPERTIES OF LEXAN
AND POLYPHENYLENE-OXIDE PPO

Material	History	Rupture		Yield	
		Stress, psi.	Strain, in in.	Stress, psi.	Strain, in in.
Lexan	Control	2860	0.58	3560	0.08
	Exposed	3800	0.14	--	--
PPO	Control	6560	0.075	--	--

Notes:
1. All tests were conducted at a crosshead rate of 0.02 in/min and at a temperature of 125 °C.
2. Test specimens were dogbone shapes; 0.005-inch thick, 0.125-inch width, 0.8-inch test length. Strain was calculated on the basis of an 0.8-inch effective gage length.
3. Lexan control data based on average of duplicate tests; remaining data based on average of four tests.
4. Lexan exposure conditions were as indicated for SE-3613 and -3713 in Table XVII.

Table XX

EFFECT OF VACUUM-THERMAL ENVIRONMENT
ON TENSILE PROPERTIES OF HYCAR AND SILICONE RUBBERS

Material	History	Test Temp., °C	Stress at Strain of 0.25, psi	Stress at Rupture, psi	Strain at Rupture, in./in.
Hycar-1	Control	25	95	1180	1.87
	Exposed	25	166	990	1.01
	Control	125	75	385	0.97
	Exposed	125	155	404	0.52
Hycar-3	Control	25	104	1240	1.31
	Exposed	25	184	980	0.68
	Control	125	108	435	0.72
	Exposed	125	192	505	0.40
SE-555 Red	Control	25	65	825	4.17
	Exposed	25	84	760	2.86
	Control	125	53	310	1.92
	Exposed	125	77	311	1.29
SE-3604	Control	25	109	637	1.04
	Exposed	25	131	662	1.04
	Control	125	112	405	0.65
	Exposed	125	125	463	0.68
SE-3613	Control	25	87	422	0.88
	Exposed*	25	104	358	0.68
	Control	125	98	253	0.61
	Exposed*	125	116	190	0.40
SE-3713	Control	25	165	760	1.06
	Exposed*	25	195	643	0.79
	Control	125	168	546	0.84
	Exposed*	125	201	440	0.58

Notes:
1. All data points are averages of measurements on duplicate specimens. * indicates average of tests in triplicate.
2. Tests were conducted at an extension rate of 0.1 in./min.
3. Control specimens were stored at normal room conditions for the entire period from specimen preparation to final testing.
4. Exposure conditions were as indicated in Table XVII.

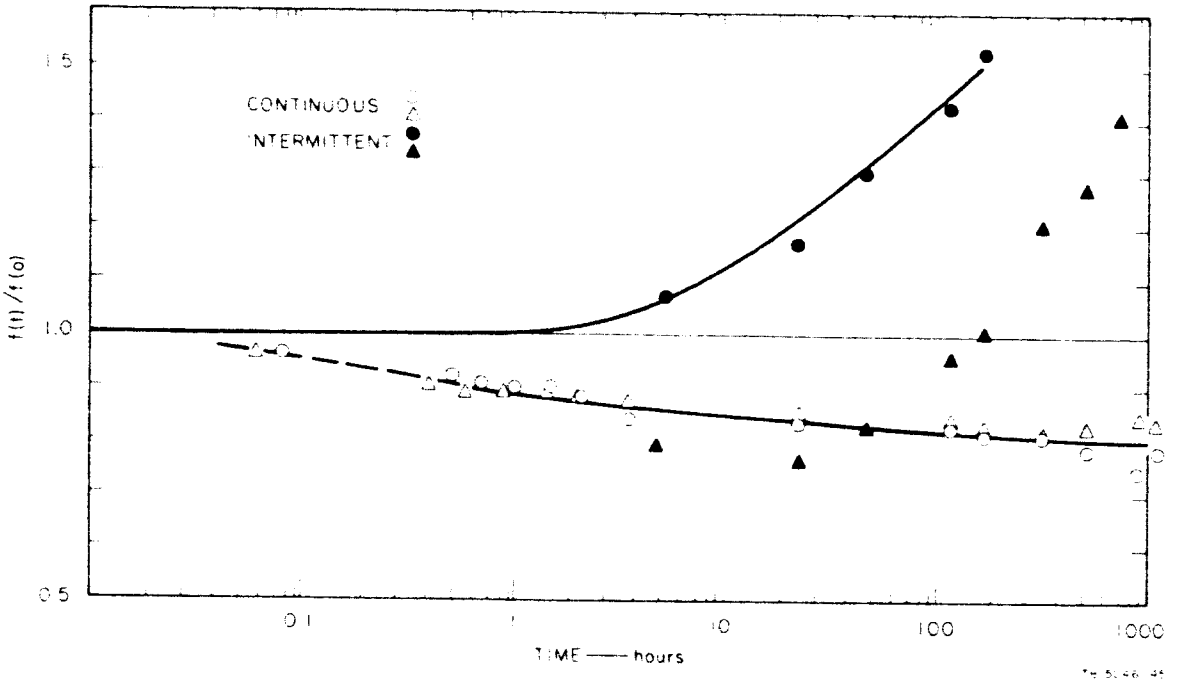

FIG. 8 CONTINUOUS AND INTERMITTENT STRESS-RELAXATION RESULTS FOR HYCAR-1 IN VACUUM AT 125°C

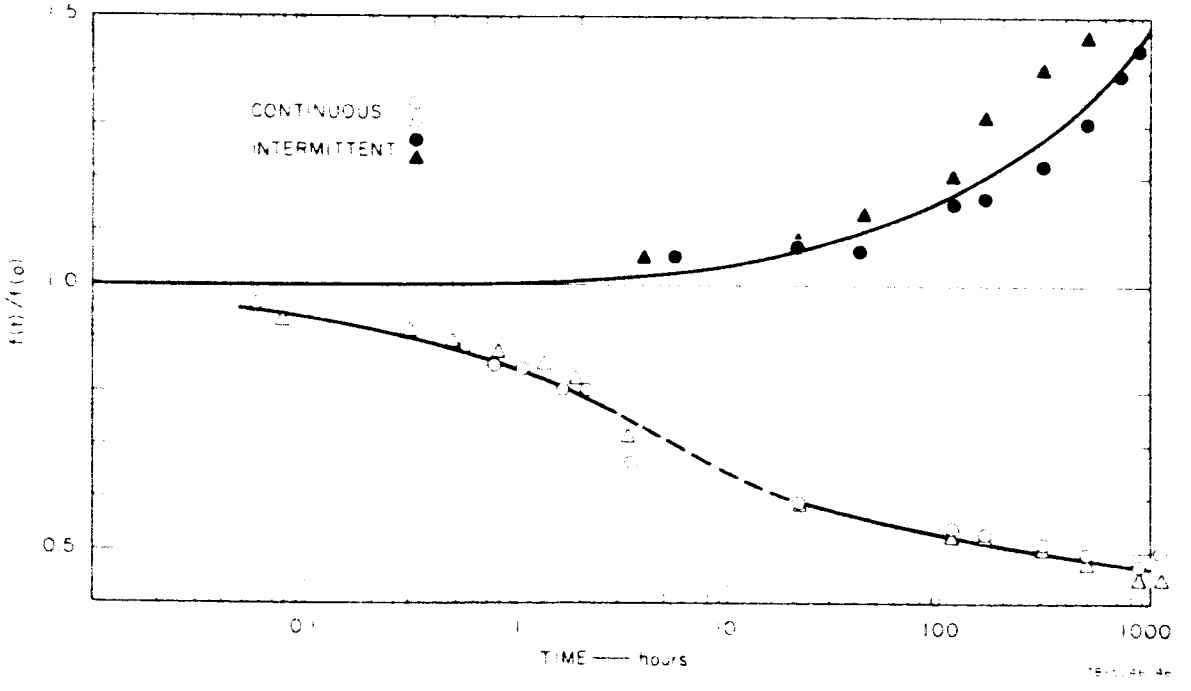

FIG. 9 CONTINUOUS AND INTERMITTENT STRESS-RELAXATION RESULTS FOR HYCAR-3 IN VACUUM AT 125°C

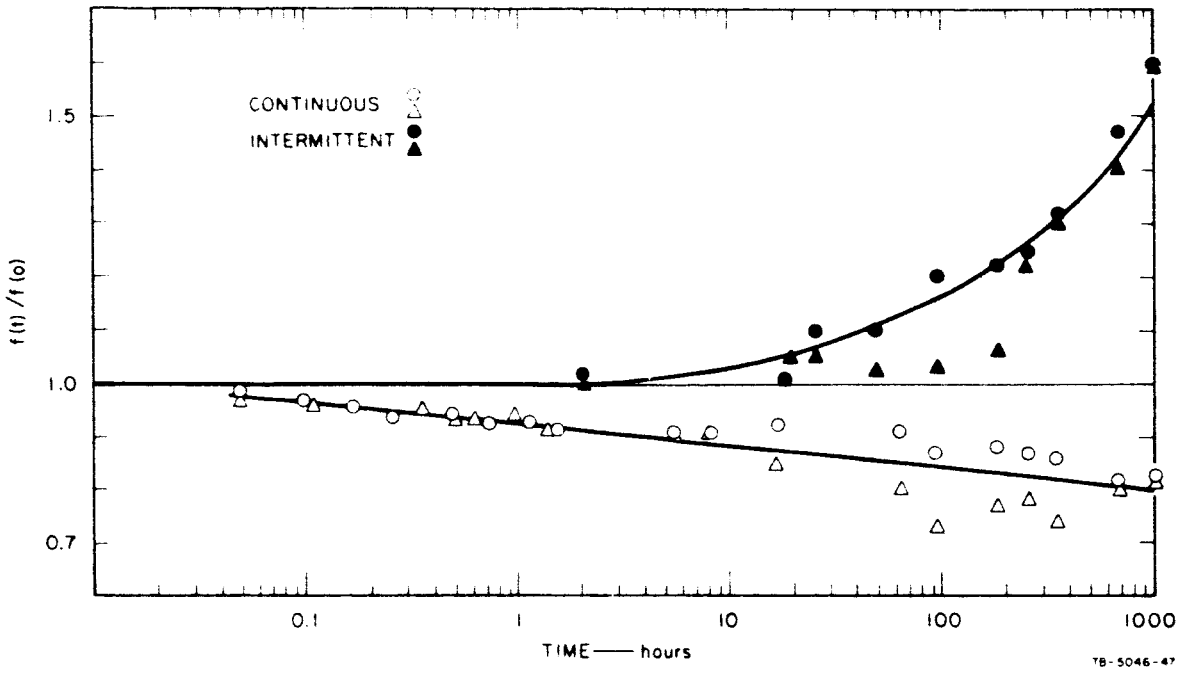

FIG. 10 CONTINUOUS AND INTERMITTENT STRESS-RELAXATION RESULTS FOR SE-555 IN VACUUM AT 125°C

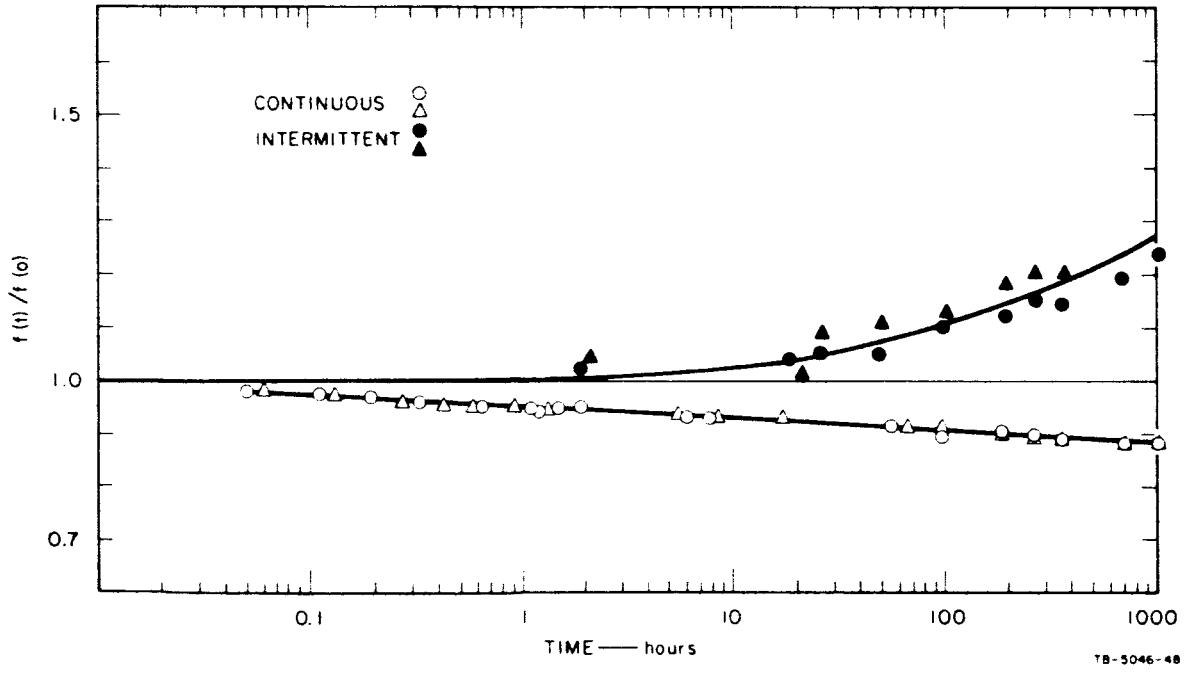

FIG. 11 CONTINUOUS AND INTERMITTENT STRESS-RELAXATION RESULTS FOR SE-3604 IN VACUUM AT 125°C

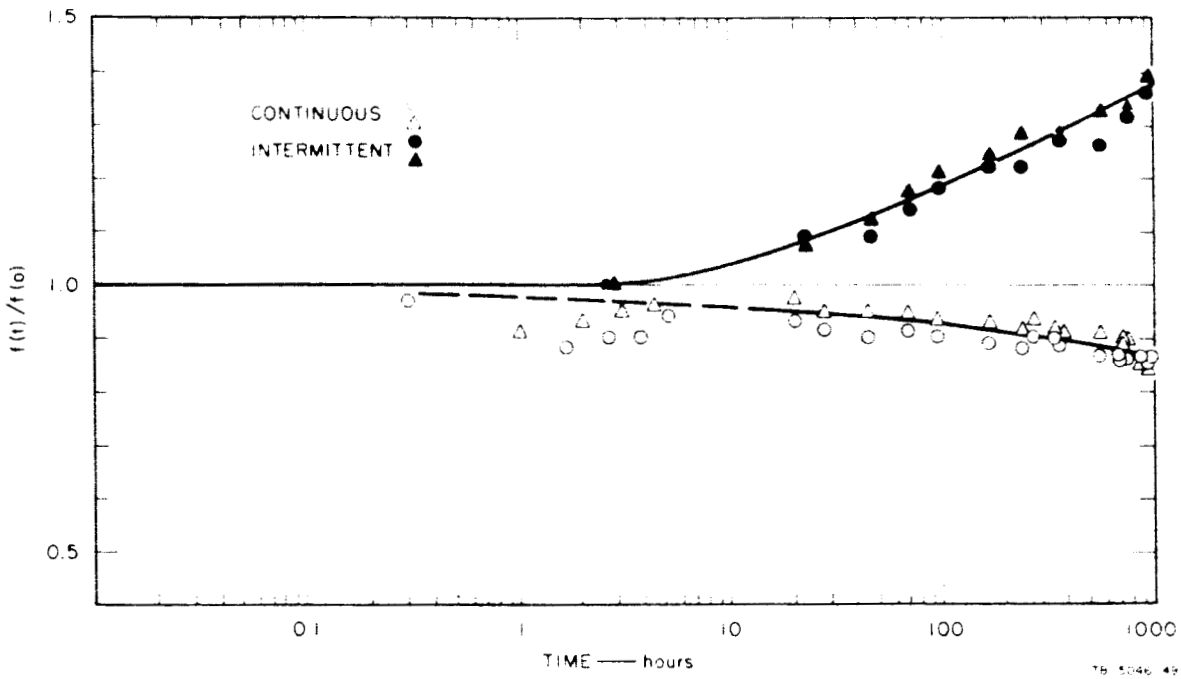

FIG. 12 CONTINUOUS AND INTERMITTENT STRESS-RELAXATION RESULTS FOR SE-3613 IN VACUUM AT 125°C

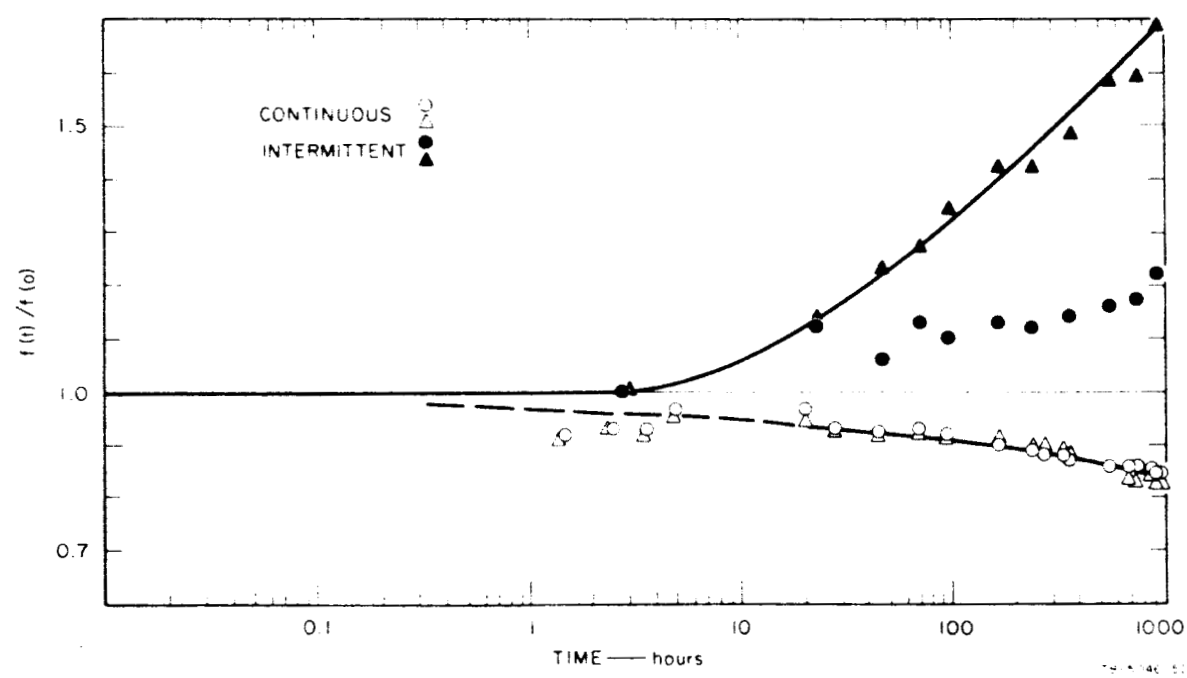

FIG. 13 CONTINUOUS AND INTERMITTENT STRESS-RELAXATION RESULTS FOR SE-3713 IN VACUUM AT 125°C

B. EIGHT-MONTH STORAGE TESTS OF SELECTED POLYMERS

Since much of the evaluation in a thermal-vacuum environment of polymeric materials for spacecraft use is based on relatively short-term test methods, there is always the question of reliability of material performance in long-term exposures in actual spacecrafts, particularly when flights to the planets are of such long duration, e.g., 8 months to Mars. Therefore, one commitment of this program is to maintain observation of selected polymeric materials during an 8-month exposure to conditions of 125°C and $< 10^{-6}$ torr, for two reasons: (1) to monitor the preservation or degradation of mechanical properties, and (2) to determine the effectiveness of short-term tests in the evaluation of polymers for long-term use.

Of the materials studied thus far under this contract and under a prior contract (JPL 950324),[2] three elastomers have shown the best performance in mechanical property tests: General Electric SE-3604 (silicone), du Pont Viton A4411A-990 (vinylidene fluoride-hexafluoropropylene), and Goodrich Hycar-520-67-108-1 (polyacrylic nitrile). In discussion with the JPL Cognizant Engineer, it was decided that these materials would be subjected to different levels of constant strain for an 8-month period; the surviving materials, as well as specimens which had been stored in an unstrained condition, would be tested for tensile properties to detect whether subtle changes have occurred.

Interpretation of test results at the end of the 8-month storage period will involve comparisons of tensile properties and observations of the times-to-rupture of the strained specimens. Tensile properties for each material after the 8-month exposure to vacuum at 125°C will be compared to control and 1000-hour data to determine the approximate rate of change of properties in the 1000- to 6000-hour periods as compared to that of the first 1000 hours. Similarly, by observing the times-to-rupture during the 8-month period, determination should be possible of whether degradation of properties had diminished or increased in the time period beyond 1000 hours. Ideally, if the specimens at the largest strain will rupture during the first 1000 hours, survival of all

remaining strained specimens would indicate low or decreasing rates of degradation beyond 1000 hours. If specimens continue to rupture at successively smaller strains during the entire period, degradation rates can be assumed to be constant or increasing. If, on the other hand, no specimens rupture during the entire program, while good stability might be indicated, the lack of results would not allow meaningful inferences to be made.

Photographs of the assemblies constructed for this purpose are shown in Figures 14 to 17, and design drawings are given in Figures 18 to 25. Figure 14 shows the basic structure and the supports on which elastomeric materials (sample rings) can be placed at calculated strains.

In Figure 15 the glass cylinder heater is shown around the basic structure. The glass has been coated at SRI with a bismuth oxide-gold-bismuth oxide laminate; the gold layer is of the order of 90-100 $\mathring{A}$ in thickness. At intervals, current-carrying copper wires have been affixed to conducting silver paint which is deposited under and over the laminate; after deposition of the laminate over initial bands of silver paint, the assembly was annealed at 400°C, and then the final bands of silver paint were applied. As shown in Figure 15, clear visibility is provided through the heater.

The bell-tube (vacuum chamber) for each unit is shown in place in Figure 16 and an assembly of four units is shown in Figure 17. Aluminum shields serve a dual purpose, i.e., maintenance of thermal equilibrium and protection from radiation (fluorescent fixtures). Each unit has a separate heating control, three-position thermocouple read-out, and vacuum system. The thermocouple beads are inserted in pieces of the same elastomer as being tested: thus, the observed temperatures at different locations within the unit is representative of the temperature of the materials under test.

Rings of each material were stretched at room temperature between support pins to the largest strains which could be sustained. In most instances, four rings were placed at each level of strain, and at least

four rings were stored unstrained as controls in each unit. Only one elastomer species is used in each unit in order to prevent cross contamination by volatilized substances.

At start-up, each unit was evacuated to less than 10^{-3} torr with a mechanical pump, and then its ion pump (Varian, 15 liter/sec) was turned on. When a pressure of less than 10^{-5} torr was indicated, each unit was permanently sealed off by crimping the fore pump line. Then the temperature of the units was raised gradually as described below.

Preliminary outgassing of the materials was accomplished at about 40°C for about 175 hours, during which time the pressure was less than 10^{-5} torr. Approximately 10 hours were required to raise the temperature from 40°C to 125°C; the pressure did not exceed 10^{-4} torr during that period. Storage time is computed from the approximate time of first exposure to 125°C, which was at about 6:00 P.M. on December 27, 1965. From 0 to 50 hours, the pressure was less than 10^{-4} torr; from 50 to 150 hours, the pressure had decreased to less than 10^{-6} torr.

Data on the number of samples at various strains in each unit and times of rupture are summarized in Table XXI for the period December 27 to February 27, 1966.

The fourth unit is being reserved for constant-load tests to be performed with a plastic material.

Table XXI

SUMMARY OF DATA FOR EIGHT-MONTH STORAGE TESTS IN VACUUM
(December 27, 1965 to February 27, 1966)

Material	Approx. Strain, in./in.	No. of Rings	Approx. Rupture Time, hrs at 125 °C
SE-3604	0	5	
(General	0.25	4	
Electric)	0.35	4	
	0.50	4	
	0.75	4	
	1.00	4	
	1.50	4	1 at -160: 1 at -7 1 at 0
Viton	0	8	
A4411A-990	0.25	4	
(Du Pont)	0.35	4	
	0.50	4	
	0.75	4	
	1.00	4	
	1.50	4	
	2.50	4	
	3.50	4	2 at -3
Hycar-1	0	4	
(B.F. Goodrich)	0.25	2	
	0.35	2	
	0.50	2	
	0.75	4	
	1.00	4	
	1.50	4	2 between 100-160 1 between 170-185

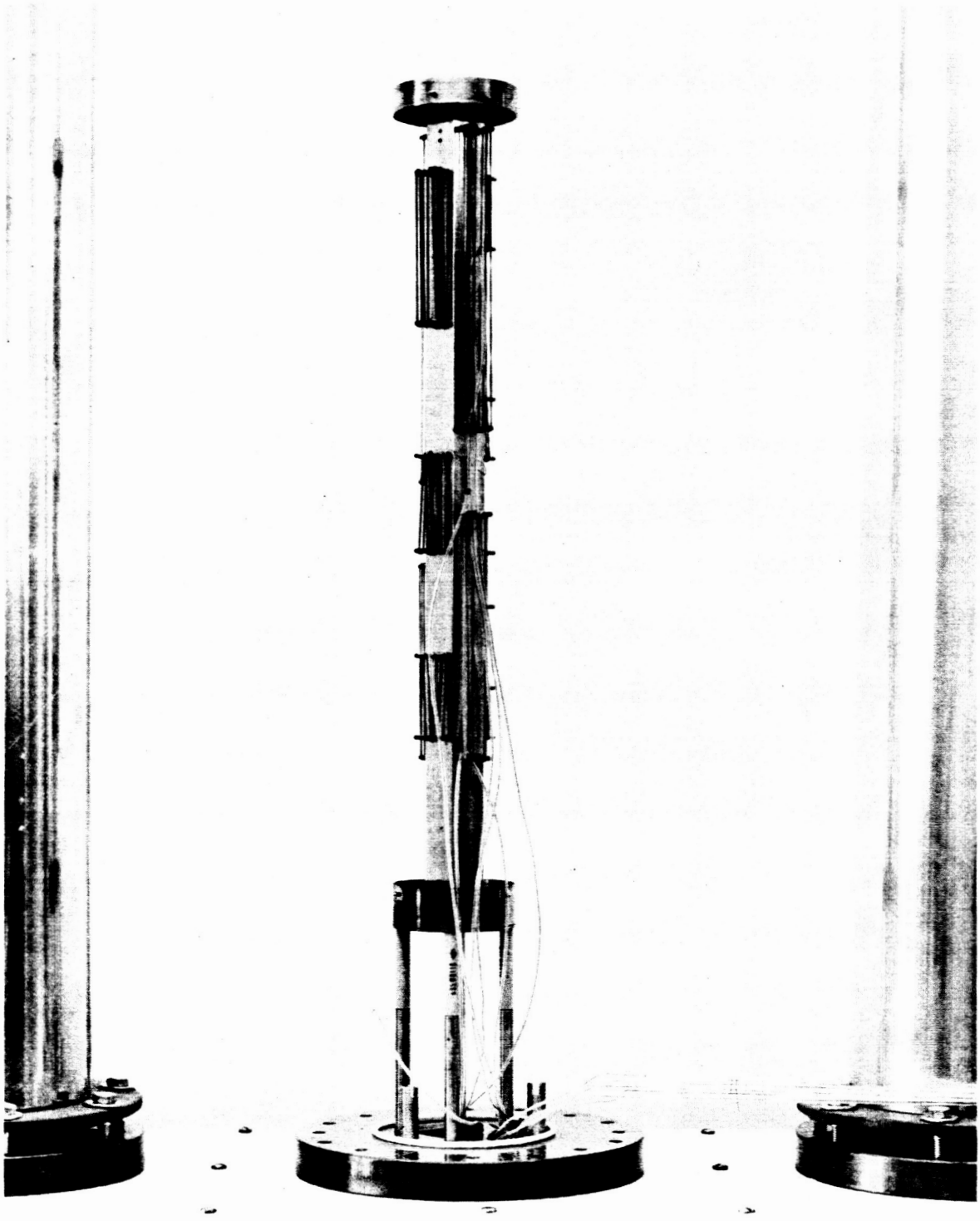

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FIG. 14 BASIC STRUCTURE FOR SUBJECTING SELECTED ELASTOMERS TO SPECIFIC INITIAL STRAINS

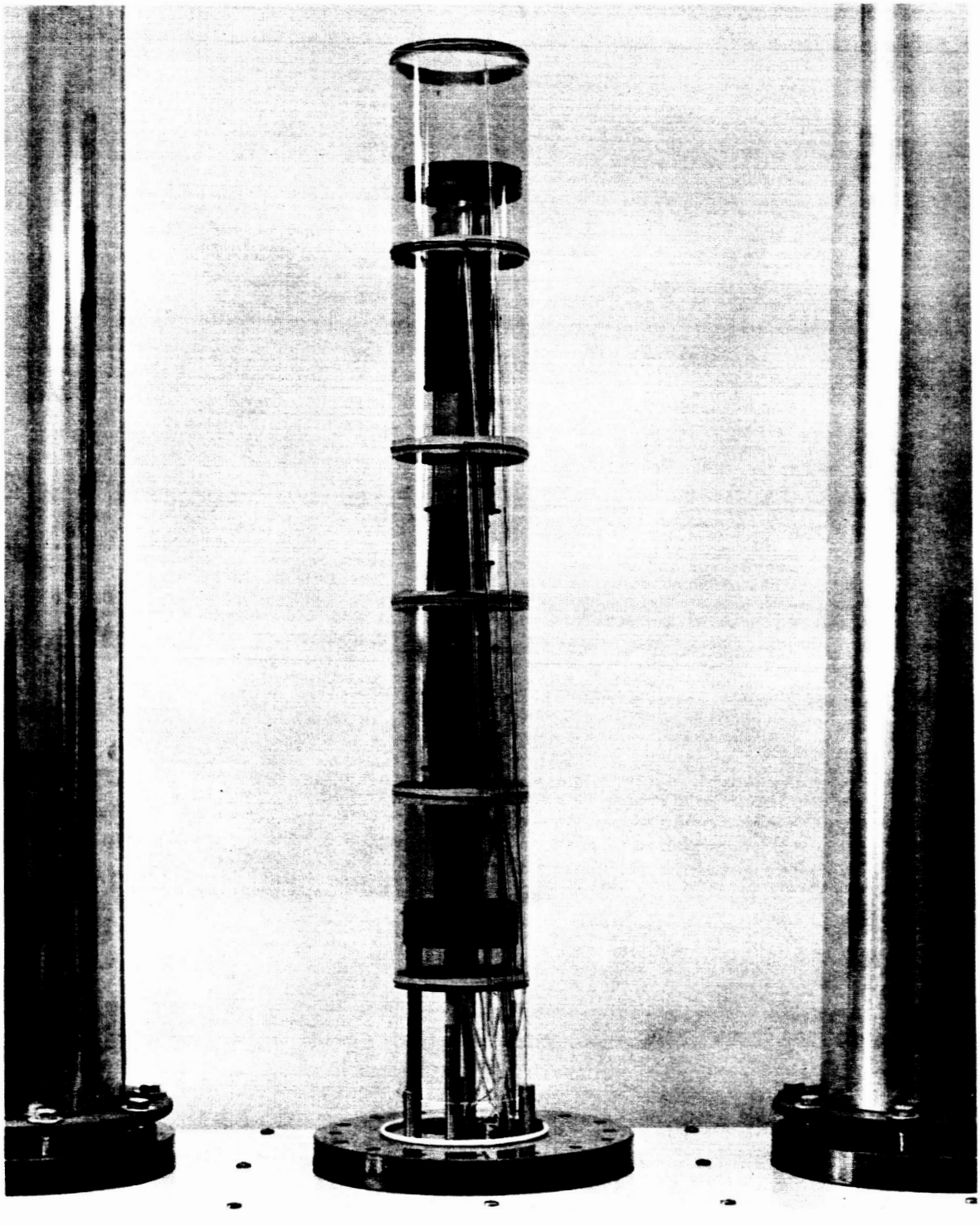

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FIG. 15 VIEW OF CONSTANT STRAIN APPARATUS WITHIN GLASS CYLINDER HEATER

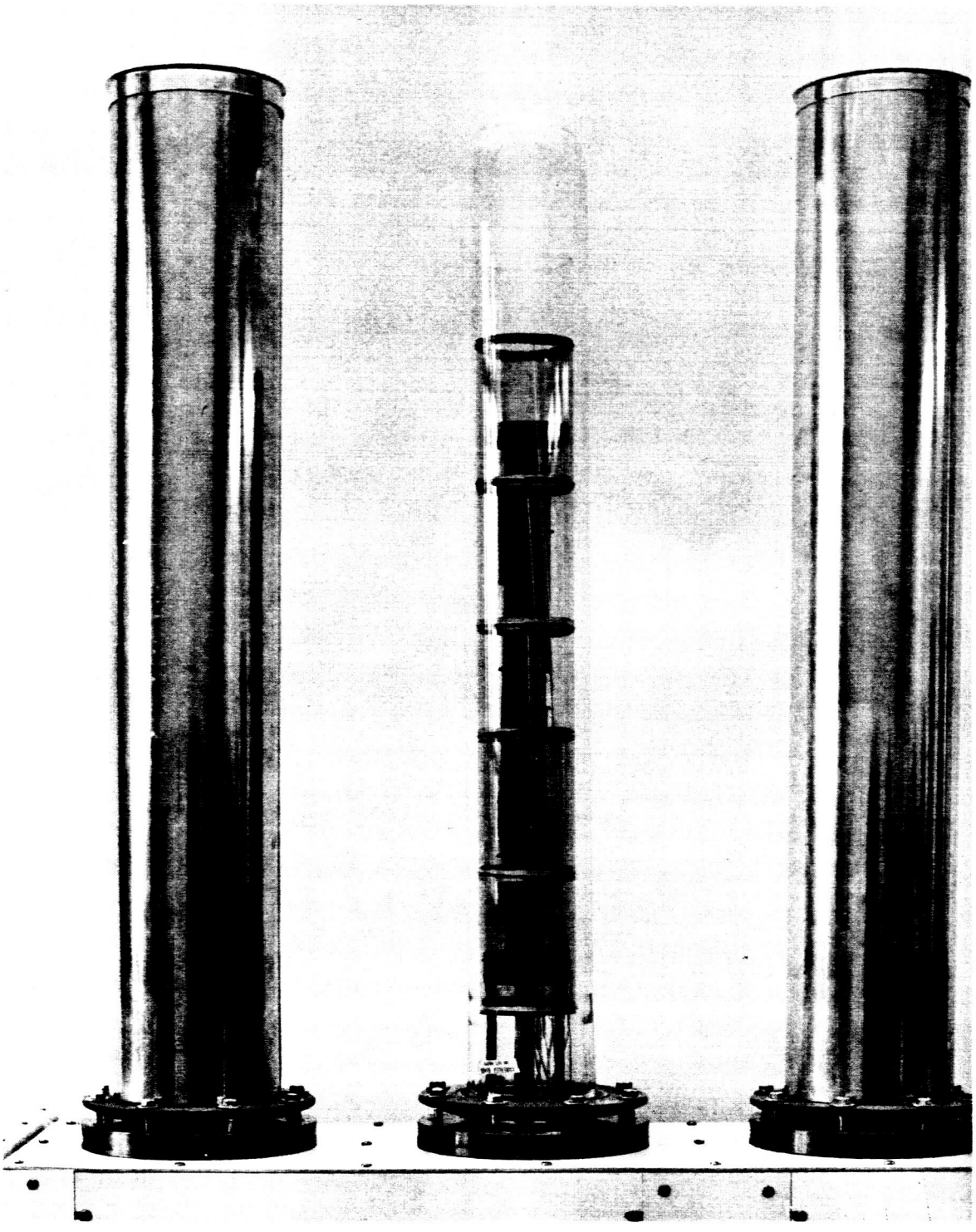

FIG. 16 VIEW OF CONSTANT STRAIN APPARATUS AND GLASS CYLINDER HEATER WITHIN BELL-TUBE

75

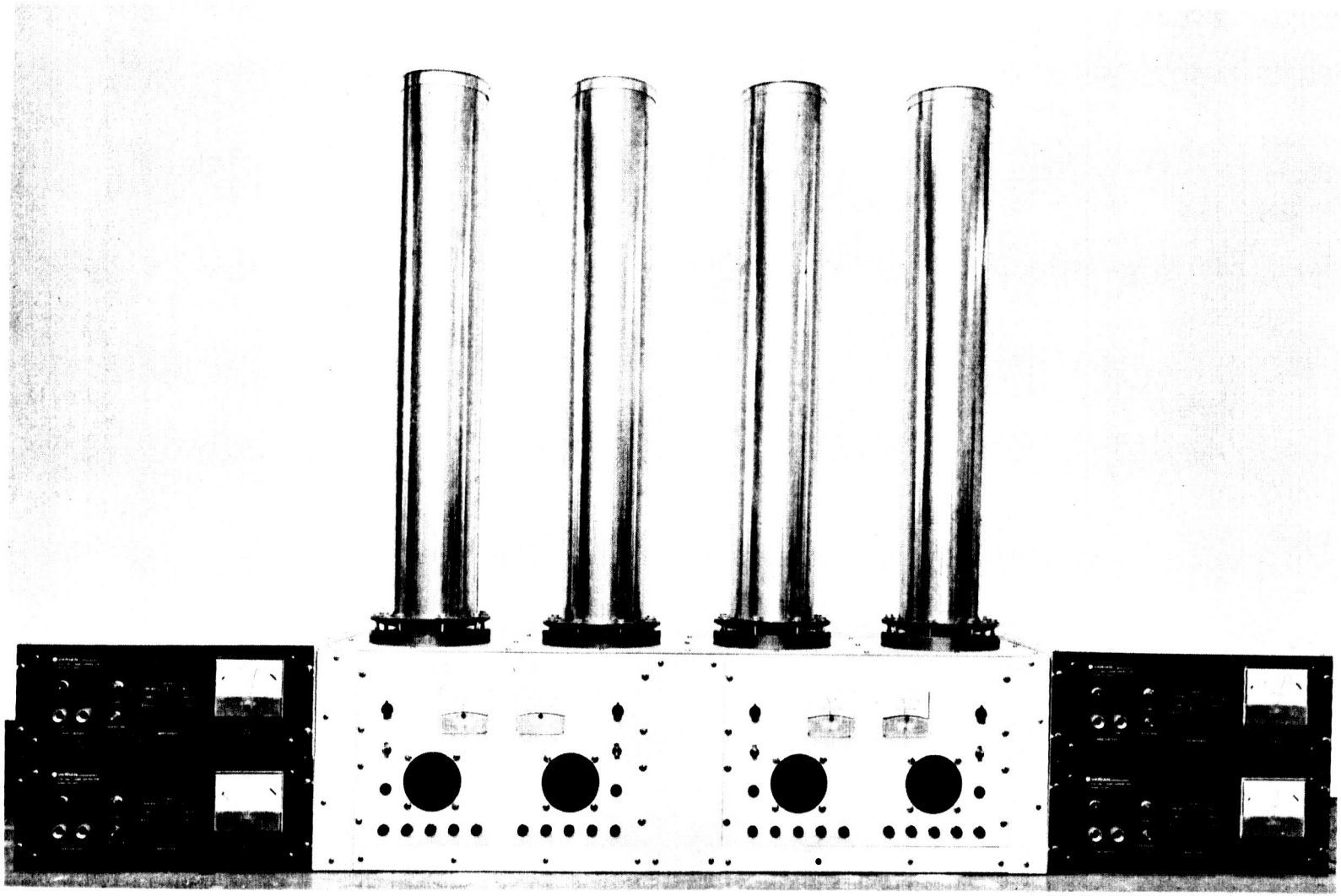

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FIG. 17 PHOTOGRAPH OF TOTAL ASSEMBLY FOR 8-MONTH THERMAL-VACUUM TESTS OF SELECTED POLYMERIC MATERIALS

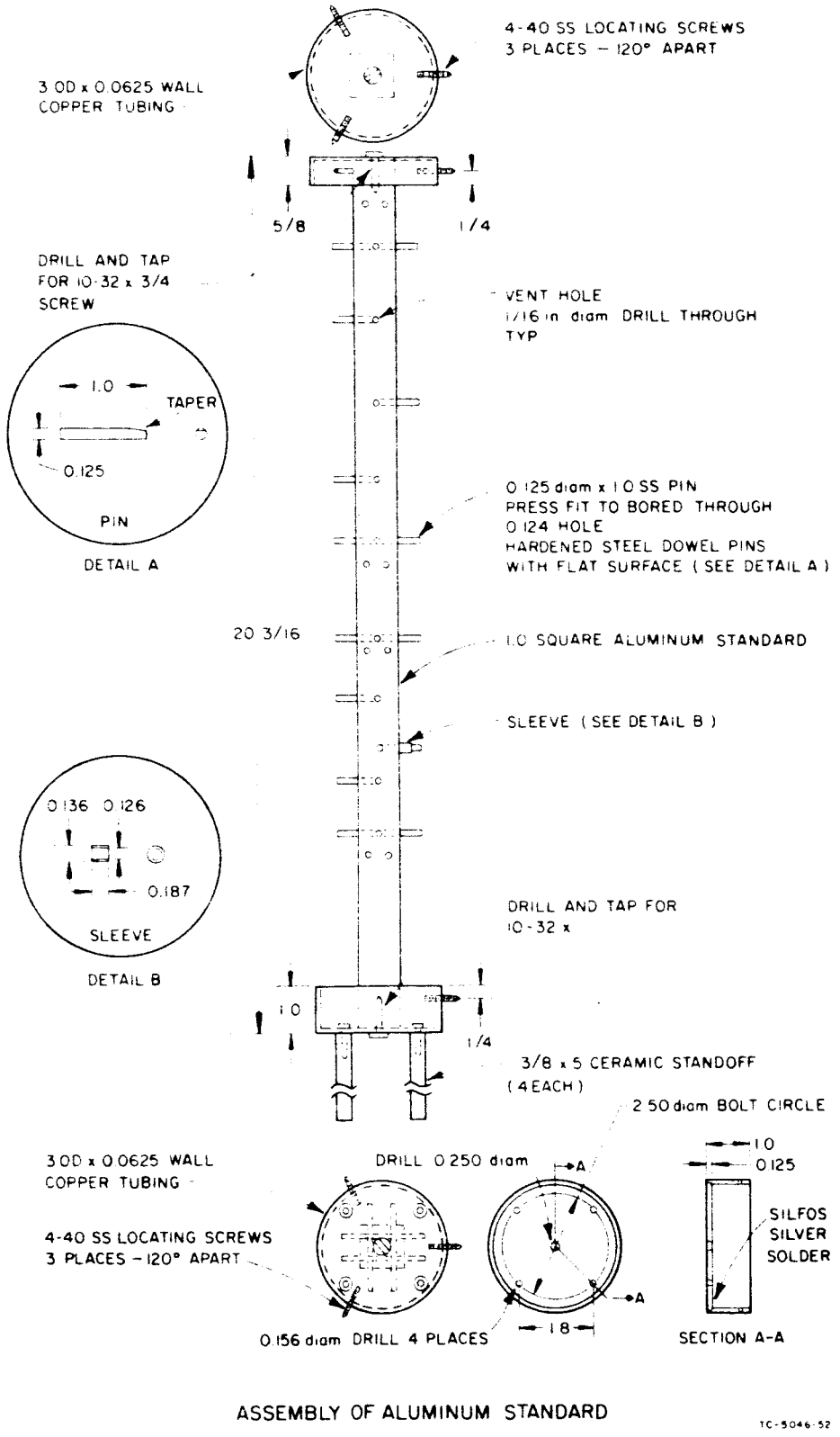


FIG. 18 DESIGN DRAWING FOR CONSTANT-STRAIN APPARATUS FOR 8-MONTH STORAGE TESTS

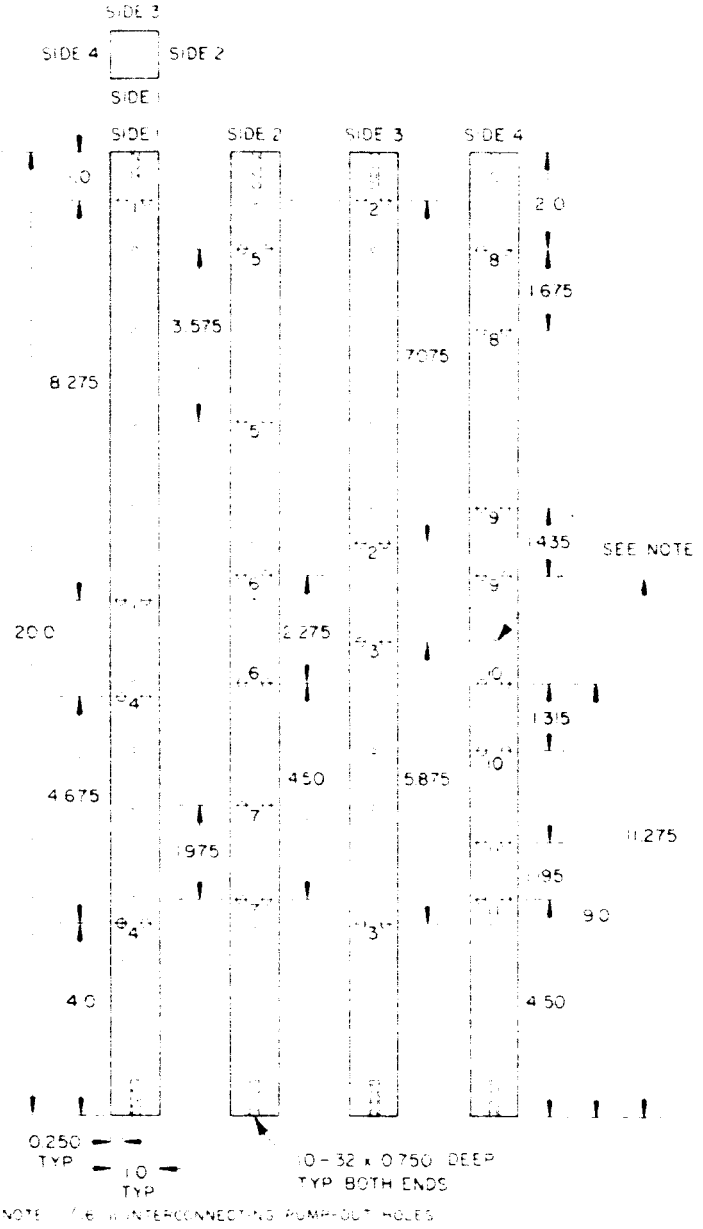
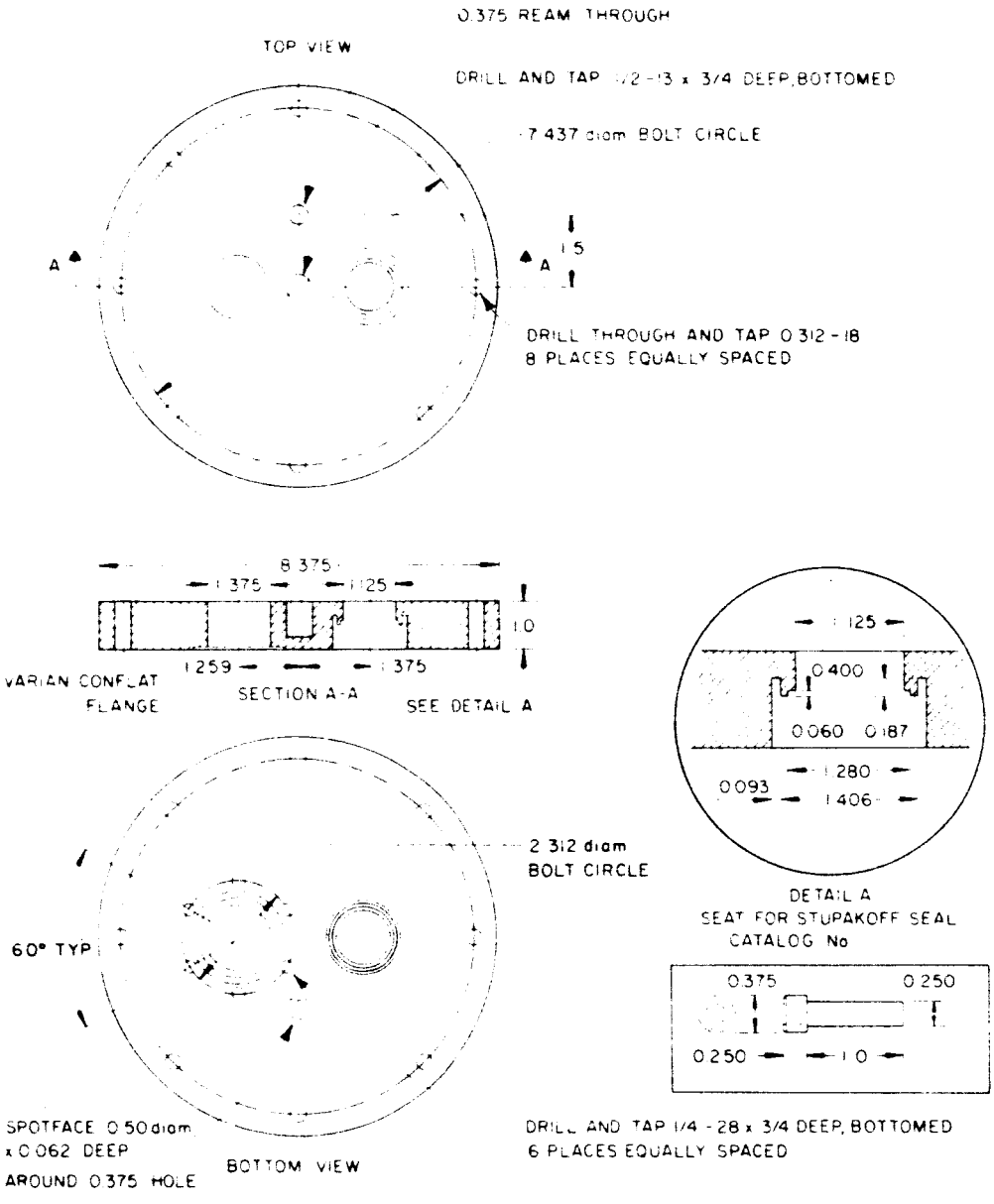


FIG. 19 DETAILED DESIGN DRAWING FOR CONSTANT-STRAIN APPARATUS FOR 8-MONTH STORAGE TESTS



VACUUM FACE PLATE

FIG. 20 DESIGN DRAWING FOR VACUUM FACE PLATE FOR 8-MONTH STORAGE UNITS

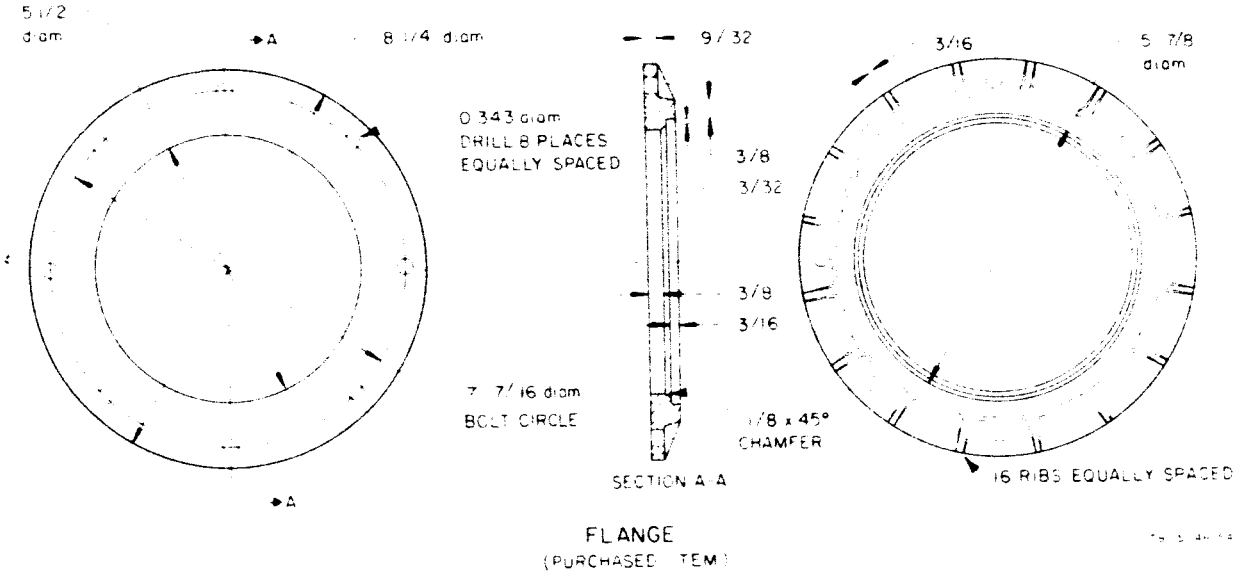


FIG. 21 FLANGE DIMENSIONS FOR 8-MONTH STORAGE TEST UNITS

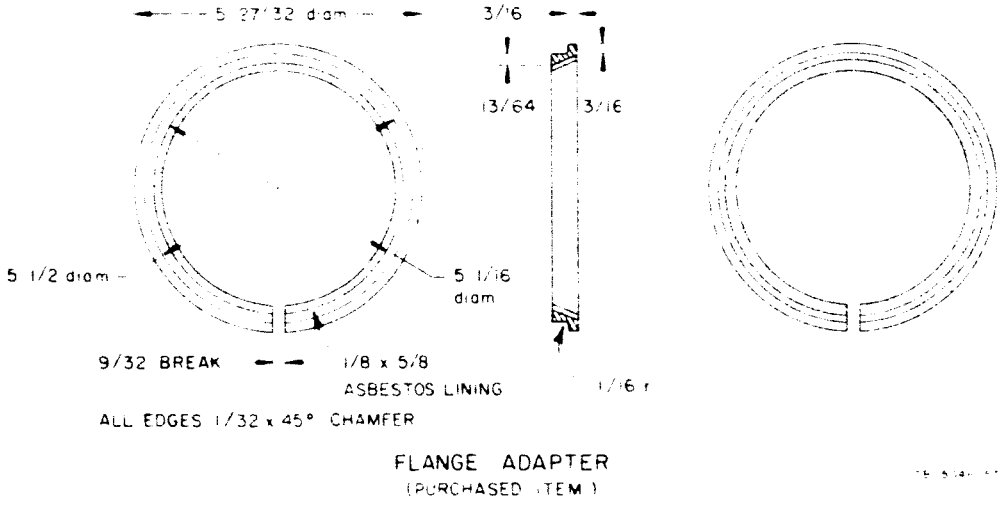


FIG. 22 FLANGE ADAPTER DIMENSIONS FOR 8-MONTH-STORAGE TEST UNITS

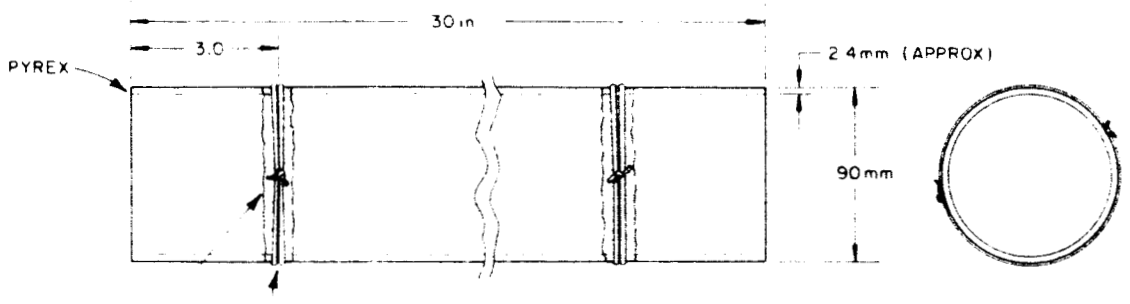


FIG. 23 DESIGN DRAWING FOR GLASS HEATER FOR 8-MONTH-STORAGE TEST UNITS

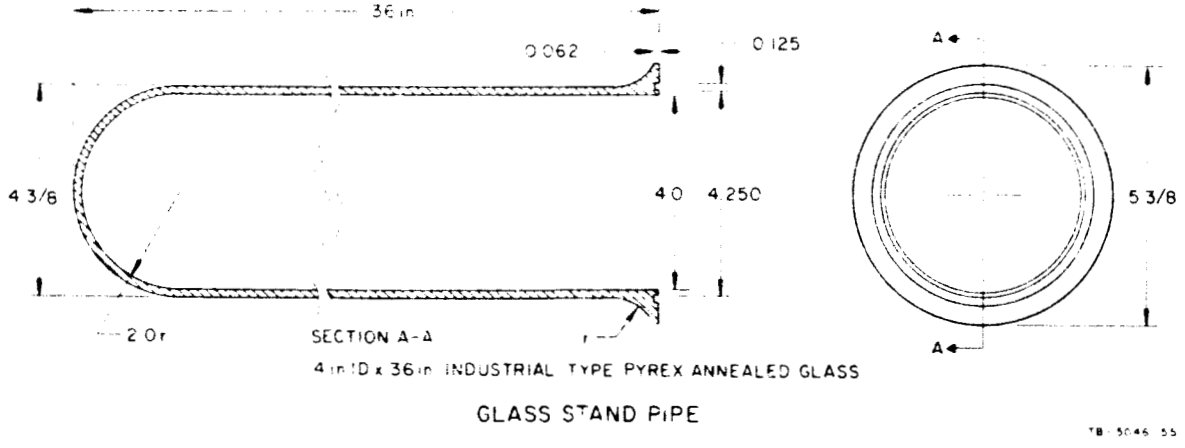


FIG. 24 DIMENSIONS OF GLASS STAND PIPE FOR 8-MONTH-STORAGE TEST UNITS

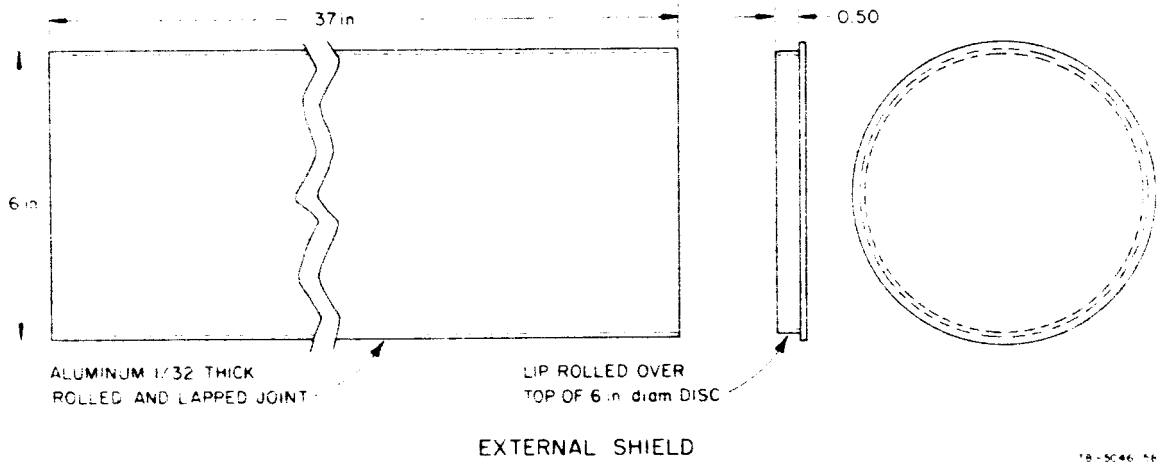


FIG. 25 DIMENSIONS OF EXTERNAL SHIELD FOR 8-MONTH-STORAGE TEST UNITS

V. VOLATILE CONDENSABLE MATERIAL

The philosophy and purpose of determinations for volatile condensable material (VCM) have been discussed at length in another report;[2] the VCM value has been defined as the weight of condensate obtainable at 25°C in a given interval of time from a unit area of material of a given thickness maintained at 125°C in a vacuum of at least 10^{-6} torr. Examples of VCM values are given in the following table for an acceptable polymer, Viton A4411A-990 (du Pont, vinylidene fluoride-hexafluoropropylene) and an unacceptable polymer, Hypalon A2211A-2718 (du Pont chlorosulfonated polyethylene).

Exposure Time, Hrs	VCM Value at 125/25°C, mg/in^2	
	Viton A4411A-990	Hypalon A2211A-2718
24	1.43	3.58
48	0.49	6.88
96	0.73	9.05
300	0.51	22.03

These data were the last to be obtained with the prototype VCM apparatus[2] which has since been dissembled for replacement by an improved VCM apparatus.

A. IMPROVED VCM APPARATUS

The prototype VCM apparatus has been shown to be entirely satisfactory for the work performed thus far; however, the application of this apparatus was limited to elastomeric sheets. Since both plastics and elastomers in various configurations, such as tie-cords, laminates, sleevings, etc., must also be evaluated, and since an increased amount of data per 4-week run for engineering curves is desirable, work

[2] Muraca, R. F., et al., "Space Environment Effects on Polymeric Materials," Stanford Research Institute, Interim Technical Report No. 2, Project 4257, May 1965.

performed during this reporting period has involved the design and fabrication of a new and more versatile apparatus.

The new units will provide for simultaneous VCM determinations for 10 to 12 samples, and may best be described as individual "clam-shells," spun from copper, with appropriate supports to accommodate any type of sample. The heating element for each clam-shell consists of X-Actiglo wire wrapped uniformly around the shells and soldered in place. The polished copper collector plates are fastened to a support cooled by soldered-in-place water lines. Fabrication of the units has been completed; a check-out run of a prototype unit has shown that the temperature of 125°C is readily maintained within the clam-shell and at the nozzle, while the collector plate is maintained at 25°C.

A pumping system of greater capacity than that used previously is required for this increased load (12 units compared to 6). Work is underway toward the design and fabrication of this system; work will be initiated on the VCM determinations as soon as the system can be assembled.

VCM Values

As described earlier, VCM values for elastomers have related to a unit area of material of a given thickness:

wt of VCM per unit area

In future work, VCM values will be defined in accordance with the configuration of the material, for example, tie-cords:

wt of VCM per unit length

Pertinent dimensions, such as width of tapes and thickness of films will be identified.

B. MICRO-VCM

A real need of both phases of this program has been for a rapid screening procedure which will expedite the selection of materials for detailed qualification tests (Phase I) and for extended evaluation (Phase II). For this reason, a multiple-unit has been designed and

fabricated which will provide within 24 hours values of the maximum VCM for 22-24 samples.

Samples of 100-200 milligrams are used with this unit; hence, these determinations are called "micro-VCM" for contrast with the VCM values previously mentioned. Since the sample weights are of the order of milligrams, the micro-VCM value reflects the maximum amount of volatile condensable substance which will be released by a polymeric material at 125°C in vacuo. (It will not illustrate the subsequent evaporation of condensed material with time, which is indicated by the VCM curves established for engineering information.) Additionally, vacuum-weight-loss determinations can be conducted concurrently.

Apparatus

The apparatus is attached via a 6-inch elbow to a high-speed vacuum system, equipped with a Welch 1397B ioropump and a CVC MCF-700 oil-diffusion pump. A pressure of 10^{-6} torr can be maintained by employ of a liquid-nitrogen trap in the system. As shown in Figure 26, the elbow is fitted with vacuum gauges and utility plugs which carry the lines for power, water cooling, and thermocouples.

The micro-VCM apparatus consists of two units, each of which are set up for 12 samples. Figure 26 illustrates the front and back of individual units. Samples are contained in individual bored-out compartments, in a solid copper block, which are covered by the copper discs shown in the front of the photograph. The heating element for the block is X-Actiglo wire which has been soldered in place at sufficient intervals to maintain uniformly a block temperature of 125°C.

Also shown in the photograph is the copper plate which holds the VCM collector plates and is cooled by soldered-in-place water lines. The screw-heads appearing between the cooling lines hold the collector plates in place; the plates are not shown in Figure 26.

The path from the sample compartments to the collector plates is defined by a hole of large size in comparison with the compartment size; cross-contamination between compartments is eliminated by insertion of an egg-crate-like baffle.

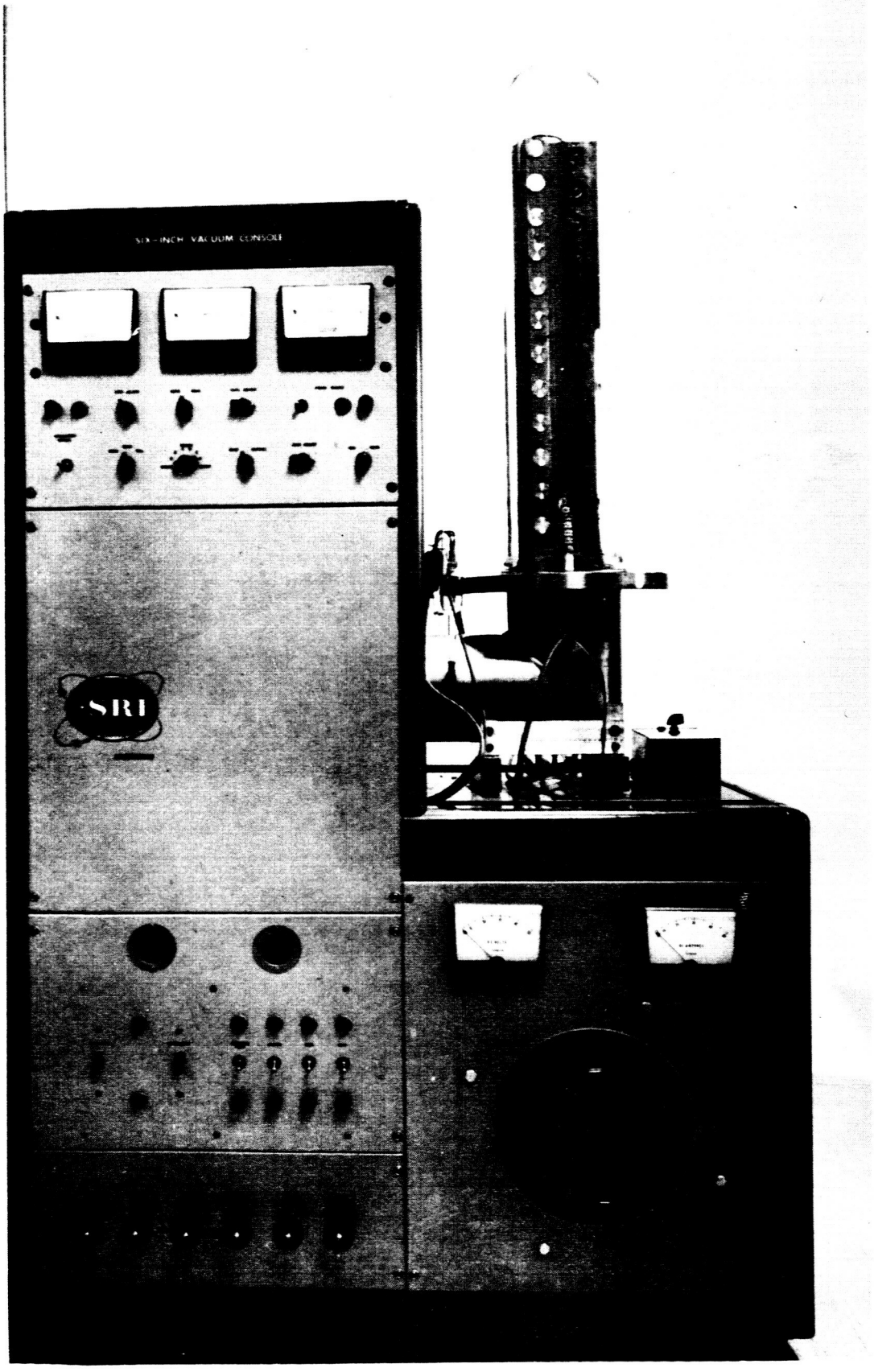


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FIG. 26 MICRO-VCM APPARATUS MOUNTED ON 6-INCH VACUUM CONSOLE

Figure 27 provides a close-up view of the micro-VCM apparatus, Design drawings of the unit are being prepared and will be published at a later date.

Procedure

Samples of 100-200 milligrams, cut in small pieces, are placed in previously-weighed micro aluminum boats and stored in an atmosphere of 50% humidity for at least 24 hours. Then the samples are weighed on a microbalance and placed in the compartments in the copper block; the compartment covers, sealed with Teflon gaskets, are secured by screws. The polished and cleaned copper collector plates are also weighed on a microbalance and fastened firmly to the copper cooling block by a screw arrangement. When the bell-jar (shown in Figure 26) has been set over the apparatus, and the system has been evacuated to a pressure less than 10^{-5} torr, the copper blocks are heated to 125°C and controlled by variable transformers. The temperature is maintained for 24 hours; then the block is allowed to cool under vacuum to at least 50°C, whereupon the bell-jar containing the apparatus is vented with dry nitrogen or helium. The samples and collector plates are removed and placed in desiccators, and weighed in order of removal from the apparatus.

The micro-VCM value is calculated on a wt-% basis (maximum VCM available); weight-loss is also calculated on a wt-% basis. The difference between the two values is reported as %-noncondensable material.

Discussion of Micro-VCM Determinations

Because of data obtained in prior work, two elastomers were selected as control samples: SE-555 (white) which has a large VCM content compared to noncondensable material, and Viton-990 which has a small VCM content compared to noncondensable material. These samples will be run with each set of determinations until an estimate of limits can be determined for the results obtained with this apparatus. Absolute and closely-reproducible values are not anticipated with this procedure,

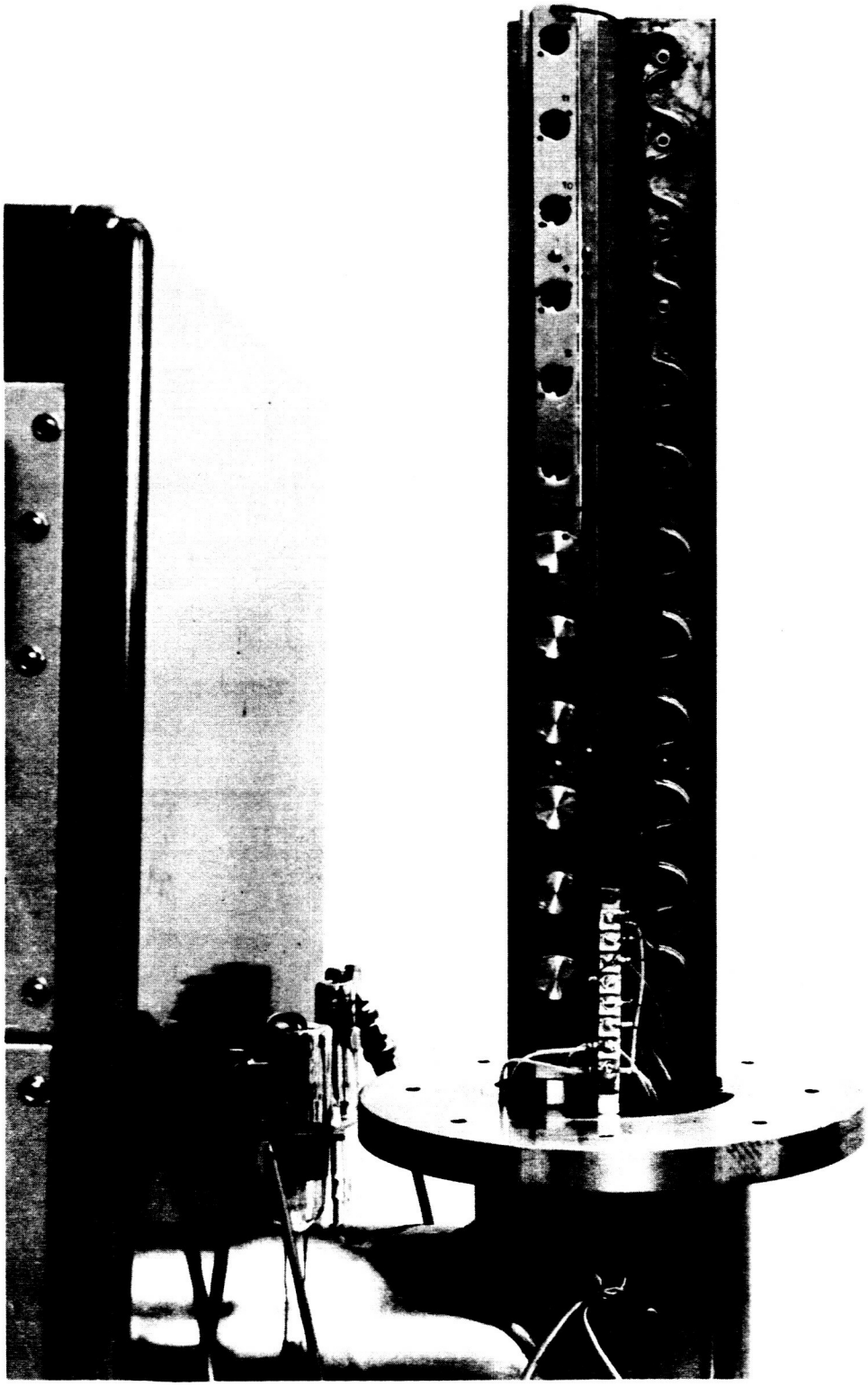

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FIG. 27 CLOSE-UP VIEW OF THE MICRO-VCM APPARATUS

since the uniformity of polymer formulations cannot be assumed when micro-sized samples are taken at random; however, it is felt that it will provide highly-satisfactory results for screening candidate materials. A summary of the results for control samples in three different runs are given in Table XXII.

TABLE XXII

MICRO-VCM DETERMINATIONS OF CONTROL SAMPLES

(24 hr at 125°C and 10^{-6} torr)
(VCM collector plates at 25°C)

Run No.	Material	Total Wt. Loss, %	VCM, wt-%	Noncondensable Wt. Loss, %
1	SE-555(white)	0.29	0.22	0.07
		0.41	0.28	0.13
2		0.78	0.43	0.35
		0.72	0.42	0.30
3		0.57	0.32	0.25
1	Viton A4411A-990	0.49	0.01	0.48
		0.53	0.09	0.44
2		0.55	0.01	0.54
		0.63	0.02	0.61
3		0.51	0.00	0.51

In general, duplicate determinations for both weight-loss and VCM values average about ± 0.06% (abs.). As shown in Table XXII, repeated determinations for the same material may show a variation of ± 0.2% (abs.) which is quite adequate for screening.

Micro-VCM and weight-loss data for the first screening runs of candidate polymeric materials are given in Table XXIII; pertinent notes regarding sample preparation are listed. Polymer classes and code names are:

Enjay Butyl	Isobutylene-isoprene, elastomers
Hycar	Polyacrylic-nitrile, elastomers
JPL-100X	Polyurethane, conformal coatings
Lexan	Polycarbonate, structural plastic
Micarta	Glass-fiber-reinforced epoxy, circuit boards (65M25 is copper-clad)
Nordel	Ethylene-propylene terpolymer, elastomers
SE-555	Silicone, elastomers

The values obtained for weight-loss agree within 0.2% of those obtained by the standardized weight-loss procedure (see Table XVI). Maximum VCM values for SE-555 (white) and Viton-990 (see Table XXII) and SE-555 (gray) (see Table XXIII) agree favorably with those obtained at 48 hours (maximum) in the prototype VCM apparatus:

Material	Prototype VCM-Value	Micro-VCM-Value
SE-555 (white)	0.56%	0.28% (av)
SE-555 (gray)	0.40	0.30 (av)
Viton-990	0.50	0.02 (av)

Exact duplication of former results was not anticipated because of the different areas used for VCM collection. In the micro-VCM apparatus, all VCM is collected directly on a collector plate of approximately twice the area used in the prototype apparatus. The increased surface area permits volatilization of material at a greater rate and thus the residuals on the micro-VCM collector plates would have a slightly different composition than in the prototype apparatus; nevertheless, a factor of two difference is observed in most instances.

An illustration of the effectiveness of the micro-VCM procedure for screening is illustrated by the results for Nordel-115: VCM values were determined previously[2] at 143°C and 93°C for 24-hr periods, with resulting values of 2.0% and 0.3%. A straight line can be drawn

Table XXIII

MICRO-VCM DETERMINATIONS[a]

(24 hr at 125°C and 10^{-6} torr)
(VCM collector plates at 25°C)

Material	Mfr[b]	Total Wt Loss, %	VCM, Wt-%	Noncondensable Wt-Loss, %	Notes[c]
Enjay Butyl EX-1090	ECC	0.80	0.24	0.56	1,3
Enjay Butyl EX-1091	ECC	0.70	0.20	0.50	1,3
Enjay Butyl EX-1092	ECC	0.86	0.10	0.76	1,3
SE-555 (Gray)	GE	0.53	0.30	0.23	1,2
Hycar-520-67-108-1	BFG	1.90	0.17	1.73	1,2
JPL-1001	AA	0.20	0.10	0.10	1,4
JPL-1002	AA	0.19	0.03	0.16	1,4
Lexan 100-111	GE	0.06	0.02	0.04	1,2
Lexan 101-111	GE	0.08	0.01	0.07	1,2
Lexan 101-112	GE	0.09	0.04	0.05	1,2
Lexan 103-112	GE	0.08	0.00	0.08	1,2
Micarta H-2497	WE	0.18	0.00	0.18	1,2
Micarta 65M25	WE	0.43	0.00	0.43	1,2
Nordel A5411A-115	DuP	1.80	1.29	0.51	1,5

a) Values are average of 2 determinations: for duplicate samples, VCM and wt-loss may vary ±0.06% abs.

b) ECC, Enjay Chemical Company
BFG, B. F. Goodrich Company
AA, Ablestik Adhesive Company
GE, General Electric Company
WE, Westinghouse Electric Company
DuP, E.I. DuPont de Nemours Company, Inc.

c) 1. Conditioned in 50% humidity for 24 hr before initial weighing, and stored in desiccator for 30 minutes before final weighing.

2. Sample used as received.

3. Postcured 4 hr at 150°C.

4. Cured 4 hr at 75°C.

5. Postcured 18 hr at 175°C.

between these points, since the VCM value is a function of the rate of evaporation at a given temperature, and a value of 1.4% can be estimated for VCM at 125°C; the micro-VCM value is 1.3%.

The maximum value for VCM at 143°C after 300 hours, for Nordel-115, was about 3.0%. Thus, a maximum value for VCM at 125°C can be estimated as 2.0%. In this comparison, the micro-VCM value at 1.3% for maximum-VCM may appear to be a little low, but it is in keeping with the differences anticipated for reasons described above, and it still indicates the unsuitability of this material for spacecrafts.

VI. VOLATILE MATERIAL

Mass spectral identification of substances volatilized from polymeric materials at 125°C in vacuo is made in correlation with the studies being performed with regard to mechanical-property measurements and VCM determinations. The procedure involves the pumping of a sample overnight at room temperature, in a modified inlet system attached to a CEC Model 21-103C mass spectrometer, to remove surface gases and moisture; then it is brought quickly to a temperature of 125°C and the evolved vapors are scanned immediately.

In view of the contrast in VCM values between Hypalon-2718 and Viton-990 (see Section V), and the fact that most of the weight-loss for the Viton was due to noncondensable material, it was interesting to examine the volatilized products. Viton-990 is a co-polymer of vinylidene fluoride and hexafluoropylene; as shown in Table XXIV, all of the components are quite volatile under these conditions. Hypalon-2718 is a chlorosulfonated polyethylene; the data summarized in Table XXV might explain the discoloration of the copper plugs, the increasing VCM values with time, and the reduction of polymer resilience during the VCM determinations.

Since degradation of mechanical properties had been reported for a Lexan film, both vacuum-weight-loss determinations (see Section III) and mass spectrometric examination were performed for Lexans (polycarbonates) of similar composition. The weight-loss was shown to be very small (0.2%); at first glance, there is little to indicate a material which would account for the loss of mechanical properties in the summary of volatile products given in Table XXVI. All of the products are easily attributable to synthetic processes. However, decomposition studies

of polycarbonates (in air and vacuum at higher temperatures)[3] have indicated that the presence of mineral acids or organic chloride in the polycarbonate apparently enhances the degradation of the material. Hydrochloric acid is formed during the process and is admittedly difficult to remove.

Table XXIV

MASS SPECTRAL IDENTIFICATION
OF SUBSTANCES VOLATILIZED FROM
DU PONT VITON A4411A-990
(125°C and 10^{-6} torr)

Identified Component	Estimated Composition, %
Water	50
Carbon dioxide	5
Benzyl ether	16
Dioctylphthalate	1
$(CF_2)_n$, to at least C_4	6
$C_nH_nF_n$, to at least C_{10}	1

[3] Lee, L. H., Am. Chem. Soc., Div. Org. Coatings, Plastic Chem., Preprints 22(2), 131 (1962).

Table XXV

MASS SPECTRAL IDENTIFICATION
OF SUBSTANCES VOLATILIZED FROM
DU PONT HYPALON A2211A-2718

(125 °C and 10^{-6} torr)

Identified Component	Estimated Composition, %
Water	73
Carbon dioxide	8
Sulfur dioxide	1
Hydrochloric acid	0.1
Unsaturated hydrocarbons, to C_{20}	10
Ester of phthalic acid	8

Table XXVI

MASS SPECTRAL IDENTIFICATION
OF SUBSTANCES VOLATILIZED FROM
GENERAL ELECTRIC COMPANY POLYCARBONATES*

(125°C and 10^{-6} torr)

Identified Component	Lexan 100-111	Lexan 101-111	Lexan 101-112	Lexan 103-112
Mixed hexanes	46%	68%	48%	14%
Substituted cyclo-hexanes	7	7	9	3
Water	28	12	28	66
Carbon dioxide	2	2	5	9
Phenol	2	4	3	3
Bisphenol-A	1	1	-	-
n-Propylamine	9	3	3	1
Hydrochloric acid	4	1	3	3
Aromatic components†	1	2	1	1

* 100-111, unstabilized; 101-111, heat-stabilized; 101-112, tinted; 103-112, heat- and UV-stabilized.

† to mol. wt. 256 for 103-112; to mol. wt. 400 for others.

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FUTURE WORK

A. MATERIAL SPECIFICATIONS

Investigations of physical and chemical properties of polymers will be conducted as required for incorporation into specifications requirements and test procedures.

Vacuum-weight-loss determinations via standardized procedures will be made on a continuing basis in order to establish limitations for specifications requirements for various polymeric materials.

Close co-operation with the JPL Cognizant Engineer will continue in the selection of material properties to be determined, in suggesting test methods for specifications, and in reviewing draft specifications.

B. ENGINEERING INFORMATION

Micro-VCM determinations will be made on a continuing basis in order to assist the Cognizant Engineers for both phases of the program in selecting materials for more detailed evaluation or characterization.

Work will continue on the fabrication and assembly of the vacuum system for VCM determinations which will be made in the clam-shell units. Determinations with the new apparatuses will be initiated as soon as an appropriate vacuum system can be assembled.

Corollary identification of volatilized substances by mass spectrometry will be made as pertinent.

Regular observations will be made of the status of the elastomers which are stored under constant strain for 8 months. The test of a plastic material under constant load will be initiated.

Work will continue on the measurements of stress relaxation changes for selected polymers during a 6-week exposure to the thermal-vacuum environment.

NEW TECHNOLOGY

In accordance with the New Technology Clause of Contract 950745 under NAS7-100, formal announcement is made of the various technologies which have been developed or advanced at Stanford Research Institute under JPL/NASA sponsorship.

(1) VACUUM-WEIGHT-LOSS APPARATUS FOR POLYMERIC MATERIALS

Innovator: R. F. Muraca

First used: July 1965

Reports: Interim Report No. 1 (August 1965)
Interim Report No. 2 (March 1966)
(Monthly Reports No. 13, July 1965, and following)

The apparatus is designed specifically for determining the thermal-vacuum weight-loss of polymeric materials in a simulated spacecraft environment. Description of the vacuum system used with the weight-loss apparatuses and a standardized procedure for determining weight-loss is also given.

(2) LONG-TERM STORAGE APPARATUS FOR POLYMERIC MATERIALS

Innovators: R. F. Muraca with N. Fishman

First used: December 1965

Reports: Interim Report No. 2 (March 1966)
(Monthly Reports No. 16, October 1965, and following)

The long-term storage apparatus, including a vacuum system, has been designed specifically for subjecting elastomeric materials to constant strain during long-term exposure to a simulated spacecraft environment. Description of the procedure for initiating the tests is also given.

A second apparatus (using the same vacuum system) is being fabricated for subjecting plastic materials to constant load.

(3) MICRO-VCM APPARATUS FOR POLYMERIC MATERIALS

Innovator: R. F. Muraca

First used: January 1966

Reports: Interim Report No. 2 (March 1966)
(Monthly Reports 17, November 1965, and following)

The micro-VCM apparatus is a multiple-unit (24 samples) designed for screening all kinds of polymeric materials in a simulated spacecraft environment. Vacuum-weight-loss and VCM (volatile condensable material) are determined concurrently. Description of the accompanying vacuum system and the procedure are also given.

(4) IMPROVED VCM APPARATUS FOR POLYMERIC MATERIALS

Innovator: R. F. Muraca

First used: (preliminary check-out only)

Reports: Interim Report No. 2 (March 1966)
(Monthly Reports No. 15, September 1965, and following)

The improved VCM apparatus is designed to provide engineering information on the deposition and subsequent removal of volatile condensable materials from all kinds of polymers exposed to a simulated spacecraft environment.

APPENDIX

SUMMARY OF POLYMERIC MATERIALS EXAMINED AND THE PROPERTIES EVALUATED

(As of February 1966)

POLYMER CLASS AND CODE NAME	MFR.*	SPACECRAFT USE	MECH.† PROP.	PHYS. PROP.	CHEM. PROP.	VAC. WT. LOSS	VCM	MICRO-VCM	VAPOR† ANALYSIS
Polyacrylic-glass fiber									
Ben Har Acryl A (BAI)	BH	Sleeving				X			
Ben Har Acryl C-2	BH	Sleeving				X			
Polyacrylic-nitrile									
Hycar 520-67-108-1	BFG	Sealant	X					X	
Hycar 520-67-108-2	BFG	Sealant	X						
Hycar 520-67-108-3	BFG	Sealant	X						
Isobutylene-isoprene									
Enjay Butyl EX-1090	ECC	Sealant	X					X	
Enjay Butyl EX-1091	ECC	Sealant	X					X	
Enjay Butyl EX-1092	ECC	Sealant	X					X	
Polycarbonate									
Lexan Film	GE	Structural plastic	X						
Lexan 100-111	GE	Structural plastic						X	X
Lexan 101-111	GE	Structural plastic				X		X	X
Lexan 101-112	GE	Structural plastic				X		X	X
Lexan 103-112	GE	Structural plastic						X	X
Epoxy									
Eccocoat EC/200	EC	Coating				X			
Eccocoat VE	EC	Coating				X			
Epon 422J	ShC	Adhesive tape			X				
Epon 917	ShC	Adhesive			X				
Epon 931B	ShC	Adhesive curing agent			X				
Epon B-3	ShC	Adhesive curing agent			X				
Epoxy-fiber glass									
Micarta H-8457	We	Circuit board				X		X	
Micarta 65M25	We	Circuit board				X		X	
Epoxy, modified									
Clear Varnish B-276	We	Coating				X			
Epoxy, silver-filled									
Eccobond Solder 56C/9	EC	Conductive solder				X			
Eccobond Solder 56C/11	EC	Conductive solder				X			
Polyethylene, chlorosulfonated									
Hypalon A2211A-2718	DuP	Sealant					X		X
Silicone									
M & T Catalyst T-12	MT	Curing agent for RTV		X	X				
RTV-11	GE	Potting compound		X	X	X			
RTV-60	GE	Potting compound		X	X	X			
RTV-560	GE	Potting compound		X	X	X			
RTV-615 A/B	GE	Potting compound		X	X	X			
SE-555 (gray)	GE	Sealant				X		X	
SE-555 (red)	GE	Sealant	X						
SE-555 (white)	GE	Sealant				X		X	
SE-3604	GE	Sealant	X			X			
SE-3613 (24/480)	GE	Sealant	X			X			
SE-3713 (24/480)	GE	Sealant	X			X			
SE-3813 (24/480)	GE	Sealant	X						
Polyurethene									
JPL-1001	Ab	Conformal coating				X		X	
JPL-1002	Ab	Conformal coating				X		X	
Vinylidenefluoride-hexa-fluoropropylene									
Viton A4411A-990	DuP	Elastomer	X				X	X	X

* Ab, Ablestik Adhesive Company
BFG, B. F. Goodrich Company
BH, Bentley-Harris Mfg. Company
DuP, E. I. duPont de Nemours Company, Inc.
EC, Emerson and Cuming, Inc.
ECC, Enjay Chemical Company
GE, General Electric Company
MT, M & T Chemical Company
ShC, Shell Chemical Company
We, Westinghouse Electric Corporation

† Measurements and analyses made *in situ*.

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